SPECTRA AND REACTIVITY OF SOME SOLID OXY-COMPOUNDS

by

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TO MY PARENTS

and

SANDRA.

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SUMMARY

The chromates (V) and (III) of a number of lanthanides have been prepared and their ultraviolet and visible (reflectance) spectra, infrared spectra and magnetic properties have been recorded and discussed. Praseodymium chromate (VI) has also been prepared and its properties examined.

The thermal decomposition of some lanthanides chromate (V) and praseodymium chromate (VI) have been studied by thermogravimetric analysis and differential thermal analysis and the temperatures at which maximum rate of decomposition occurs have been found. Partially decomposed samples of praseodymium chromate (VI) have been studied by e.s.r. spectroscopy, X-ray powder diffraction and infrared spectroscopy in an attempt to demonstrate the formation of praseodymium chromate (V) as an intermediate in the decomposition. Partially and completely decomposed samples of some lanthanide chromates (V) have been examined by X-ray diffraction, infrared spectroscopy and magnetic measurements and the decomposition product found to be the corresponding chromate (III). No evidence was found of the formation of any reaction intermediates.

The kinetics of thermal decomposition of the chromates (V) and praseodymium chromate (VI) have been studied thermogravimetrically over a range of temperatures and values of thermal activation energies for the decompositions have been determined. The value found for the decomposition of praseodymium chromate (VI) has been shown to further support the mechanism proposed for the decomposition of lanthanide chromates (VI) by Darrie, Doyle and Kirkpatrick (1967).

On the basis of the results found for the lanthanide chromates (V), a mechanism for the activation step in the decomposition of these

compounds has been proposed; involving (a) absorption of thermal energy by the chromate (V) group; (b) transfer of energy from chromate (V) group to a lanthanide ion; (c) propagation of energy by means of lanthanide ions to the surface, where decomposition takes place.

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SECTION I

PREPARATION AND PROPERTIES OF SOME CHROMATES (V) AND (III) AND PRASEODYMIUM CHROMATE (VI)

INTRODUCTION

A study of the kinetics of thermal decomposition of the chromates (VI) of lanthanum, neodymium and samarium [Darrie, Doyle and Kirkpatrick (1967)] has previously been reported and a mechanism of decomposition, based on an activation process involving a single electron transfer, was suggested. Since praseodymium lies between lanthanum and neodymium in the lanthanide series, a study of the kinetics of decomposition of praseodymium chromate (VI) has been carried out in this present work, to determine if a similar activation process applies.

The kinetics of thermal decomposition of the chromates (V) of lanthanum, samarium and neodymium have also been previously studied [Darrie (1967)] with a view to finding if the same electron transfer mechanism could be applied, as for the chromates (VI). Only in the case of lanthanum chromate (V) was agreement found between thermal activation energy and the energy of the chromate (V) charge transfer band. In the present work, the kinetics of decomposition of several more lanthanide chromates (V) have been studied and a mechanism of decomposition is proposed.

The initial section of this work deals with the preparation, structure and spectral properties of these compounds, the information obtained being used to support the proposed mechanism for the activation processes involved in the thermal decompositions.

A preparation of praseodymium chromate (VI) has been described in the literature [Schwarz (1963)], with results of thermo gravi metric analysis showing decomposition according to the equation:-

$$Pr_2(CrO_4)_3 \longrightarrow 2\ Pr\ CrO_3 + 0.5\ Cr_2O_3 + 2.25\ O_2$$

X-ray powder diffraction work [Schwarz (1963)] has indicated the formation of praseodymium chromate (V) as a thermally unstable inter-

mediate in the decomposition of praseodymium chromate (VI). The electron spin resonance spectrum of chromium (V) has been recorded in chromia-alumina systems [Poole, Kehl and Maciver (1962); Van Reijen, Cossee and Van Haren (1963)]; and of the chromate (V) ion as an alkaline glass at 20° K [Carrington, Ingram, Schonland and Symons (1956)]. dÅ spacings for the chromates (VI) of lanthanum and samarium have previously been reported [Darrie (1967)] and the infrared and ultraviolet absorption spectra of the chromates (VI) of lanthanum, samarium and neodymium have been measured [Darrie, Doyle and Kirkpatrick (1967)].

The chromates (V) of the lanthanides have been prepared by heating an evaporated aqueous suspension containing the stoicheiometric amounts of lanthanide (III) oxide and chromium (VI) oxide [Schwarz (1963)], or a stoicheiometric mixture of hydrated lanthanide (III) and chromium (III) oxides [Schwarz (1963)] or a stoicheiometric mixture of lanthanide (III) and chromium (III) nitrates in O_2 at temperatures below 640°C [Schwarz (1963); Bertaut, Buisson and Mareschal (1964)]. Lanthanum chromate (V) [Schwarz (1963)] has the monoclinic Huttonite structure (space group $P2_1/n$ - C_{2h}^5) [Pabst and Hutton (1951)], while the other lanthanide chromates (V) [Bertaut et al. (1964); Schwarz (1963)] have the tetragonal zircon structure (space-group $I4_1/and$ - D_{4h}^{19}) [Hassel (1926)]. The single exception is praseodymium chromate (V) which has a mixture of Huttonite and zircon structures. At temperatures above 640°C, the lanthanide chromates (V) decompose [Schwarz (1963); Bertaut et al. (1964)] in a single stage corresponding to the equation:-

$$Ln\ CrO_4 \longrightarrow Ln\ CrO_3 + 0.5\ O_2$$

i.e. with loss of oxygen and formation of chromates (III). Differential thermal analysis results and the infrared and ultraviolet

absorption spectra of the chromates (V) of lanthanum, neodymium and samarium have also been previously reported [Darrie (1967)].

The preparation of lanthanide chromates (III) by solid state reaction between the appropriate lanthanide oxide and chromium (III) oxide has been reported [Ruggiero and Ferro (1955); Schneider, Roth and Waring (1961)]. Ruggiero and Ferro (1955) reported these compounds as having the ideal cubic perovskite structure (space group O_h^1 - P m3m) or a very slightly distorted modification of this. Schneider et al. (1961) have reported the crystalline form as being an orthorhombically distorted perovskite structure (space group P bnm - D_{2h}^{16}). Lanthanum chromate (III) has been shown to have the ideal cubic perovskite structure, while samarium chromate (III), has the orthorhombic modification of this [Darrie (1967)]. The infrared and ultraviolet absorption spectra of the chromates (III) of lanthanum and samarium have been measured [Darrie (1967)], while Matveichuk, Shevchenko and Skripchenko (1966) have reported infrared absorption measurements on the complete series of lanthanide chromates (III).

Magnetic measurements on lanthanide chromates (III) have shown [Aleonard, Pauthenet and Rebouillat (1966)] these compounds to contain a lattice of anti-ferromagnetic Cr^{3+} ions and another lattice of anti-ferromagnetic lanthanide ions with only very weak lanthanide - chromium interactions. It has further been observed [Bertaut (1964)] that in the chromates (III) of the holmium and erbium the observed spin of chromium (III) was 10-30% less than that of the free ion due to the effects of covalence.

EXPERIMENTAL METHODS

The chromates of the following lanthanide ions:- Pr^{3+}, Gd^{3+}, Ho^{3+}, Er^{3+}, Dy^{3+}, Tb^{3+} and Yb^{3+} as well as Y^{3+} were prepared using the method described by Schwarz (1963), [also Bertaut et al. (1964)] which involves heating a stoicheiometric mixture of the lanthanide nitrate and chromium (III) nitrate at 590-600°C in an oxidising atmosphere. The rare earth nitrates were prepared by dissolving the corresponding rare earth oxide in nitric acid at a temperature less than 90°C. The chromium (III) nitrate was obtained by evaporation of approximately 1 M aqueous chromium trioxide solution with concentrated hydrochloric acid, followed by evaporation with concentrated nitric acid. To ensure good mixing, the lanthanide and chromium(III)nitrates were combined in aqueous solution and further evaporated to a syrup, which was placed in a platinum crucible and dehydrated at 300°C before being introduced into a furnace at 590-600°C. The oxygen required for the preparation was passed into the furnace through a 1/4 inch diameter silica tube which extended into the mouth of the crucible. All samples were heated for 10 hours at 590-600°C, with removal for re-grinding after 2,4 and 8 hours heating, and the products found to be dark-green powders.

The lanthanide oxides used in preparation of the nitrates were B.D.H. reagents of the type Ln_2O_3 of quoted 99.9% purity - were normally used without further treatment. However in the case of Pr^{3+}, the oxide as supplied was Pr_6O_{11} and it was found necessary to reduce this to Pr_2O_3 before a satisfactory preparation could be obtained. The Pr_2O_3 was prepared by reduction of Pr_6O_{11} in a stream of hydrogen at 660°C [Gruen et al. (1951)]. No such problem was encountered in the case of terbium chromate (V) where the starting material was Tb_4O_7.

The chromates (III) of Pr^{3+}, Gd^{3+}, Ho^{3+}, Er^{3+}, Dy^{3+}, Tb^{3+}, Yb^{3+} and Y^{3+} were prepared by the method described by Ruggiero and Ferro (1955), which involved solid state reaction of a stoicheiometric mixture of the lanthanide oxide and chromium (III) oxide. The reactants were ground together in an agate mortar, then pelletted in approximately 1 grm. quantities in a Perkin-Elmer 13 mm. die at a pressure of 10 tons per square inch for 5 minutes. The pellets were placed in a platinum boat and heated in the atmosphere, first at 1200°C for 30 minutes and then at 1000°C for a further 24 hours. To ensure complete reaction, each sample was removed twice during the period of heating for cooling, re-grinding and re-pelletting.

In the preparation, characterisation and study of the compounds prepared, a variety of physical techniques were employed and a short description of these is given below. For heating in air at 1200°C, a tubular furnace fitted with an Ether Transitrol Temperature controller; while under similar conditions at 1000°C, a Gallenkamp electric muffle furnace, fitted with a Gallenkamp Pyromaxim electronic controller, was used. For the preparation of lanthanide chromates (V) at a temperature of 590-600°C, a Gallenkamp furnace fitted with an A.E.I. Resistance Thermometer Controller was used, the temperature being read with an accuracy of $\pm$ 5°C from a calibrated Doran Thermocouple Potentiometer.

For thermogravimetric analysis (T.G.A.), the instrument used was a Stanton Massflow M.F.H.I. automatic recording thermobalance which provides a heating rate of 6 centigrade degrees per minute up to a maximum temperature of 1400°C. The accuracy of the instrument was checked periodically using samples of calcium oxalate monohydrate which by the nature of its decomposition gives a check at three different regions on the temperature scale. The temperatures at which

the different stages of decomposition occurred were reproducible to $\pm 5^{\circ}C$.

X-ray powder diffraction patterns were obtained using a Phillips vacuum sealed X-ray tube with a P.W. 1051 powder diffractometer. With this instrument, the source is a copper target used in conjunction with a nickel filter so that only copper K_{α} radiation [wavelength 1.5418 Å] is produced. The technique used here was to mount the sample on a film of vaseline spread on a strip of adhesive tape and the samples were scanned at a rate of 2 degrees per minute. The instrument was calibrated using a silicon disc and the accuracy in 2θ values found to be $\pm 0.2^{\circ}$ (θ being the diffraction angle). The intensities of lines were calculated relative to the strongest peak taken as 100.

CALIBRATION OF DIFFRACTOMETER WITH SILICON SAMPLE

$2\theta^{\circ}$		dÅ	
Measured	Literature	Measured	Literature
28.6	28.44	3.12	3.138
47.6	47.4	1.910	1.920
56.3	56.14	1.634	1.638

Reference:- A.S.T.M. 5-0565

Ultraviolet and visible spectra of solids were measured by diffuse reflectance using a Unicam S.P.500 spectrophotometer with an S.P. 540 diffuse reflectance attachement. In this technique, the sample is mounted below the source of monochromatic light and the light reflected from the flat surface of the sample is directed to a photocell by means of a spherical mirror. The intensity of absorption is determined by comparison of the intensity of light reflected from the sample surface with the intensity reflected from a

reference surface. In the present work, the reference material used was magnesium oxide [Griffiths et al. (1959)] - previously ignited at 1000°C to remove volatile impurities - which gives no absorption in the region under consideration. Measurements were recorded in the range 1000-250 nm. To prepare samples for study, both test and reference samples were ground for 20 minutes, placed in sample holders and excess material removed using a rubber bung, leaving a flat smooth surface.

For the measurement of Infra-red spectra, three different instruments were used. Initially a Perkin-Elmer 237 double-beam recording spectrophotometer was used to cover the range 4000-650cm^{-1} and the double-beam Perkin Elmer 137 model for the range 800-400cm^{-1}. Later spectra were recorded on a Perkin-Elmer 437 spectrophotometer - suitable for use in the range 4000-250cm^{-1}. Spectra were measured using both Mujol Mull and potassium bromide disk techniques. Nujol mull spectra were recorded using polished potassium bromide plates, separated by a 0.001 inch lead spacer. Samples for KBr disk spectra were prepared by mixing the test material (approximately 0.5% by weight) with spectroscopic grade potassium bromide (passing 300 mesh and dried at 140°C). The mixture was ground thoroughly and pressed under vacuum in a Perkin-Elmer 13mm. die at a pressure of 10 tons per square inch for five minutes.

Room temperature magnetic susceptibilities were measured by the Gouy method using a Newport Instruments 4 inch water-cooled electromagnet, which allows examination at different field strengths, and a Stanton S.M. 12 semi-micro balance for recording weight changes. With this method, the sample is placed in a glass tube which is suspended vertically between the poles of the magnet such that the bottom

of the sample tube is on a level with the centres of the pole-faces. Measurements, where possible, were made at five different field strengths. The sample tube was calibrated using mercury (II) tetrathiocyanocobaltate [Figgis and Nyholm (1958)] which has a gramme susceptibility of 16.44 x 10 c.g.s.u. at 20°C and susceptibilities and effective magnetic moments calculated as described by Figgis and Lewis (1960).

Electron spin resonance measurements were made using a Hilger and Watts Microspin E.S.R. 5 spectrometer which was fitted with a Newport Instruments water-cooled, rotateable magnet with 8 inch pole-faces, supplying a field in the region of 33,000 gauss. The magnetic field could be varied by either 50 Hz or 1000 KHz modulation and was calibrated by a proton resonance method. The instrument was of the X-band type, operating at a frequency around 9,400 MHz and samples examined using the Hilger and Watts W932 general purpose cavity. A Hilger and Watts FA999 variable temperature unit was also available to permit operation in the temperature range -200 to +160°C.

CHARACTERISATION OF SAMPLES

The chromates (V) of the lanthanides and yttrium were characterised by chemical analysis and by comparison of X-ray diffraction data with previously quoted values [Bertaut et al. (1964)]. The chromates (III) of the lanthanides and yttrium were characterised by X-ray diffraction data only.

An approximately 0.2 grm. sample of the chromate (V) was dissolved in 20 ml. volumes of 2N hydrochloric acid whereupon disproportionation occurred [Scholder (1952)] according to the equation:-

$$3\ CrO_4^{3-} + 8H^+ \longrightarrow 2\ CrO_4^{2-} + Cr^{3+} + 4M_2O$$

The chromium (VI) content of the solution was determined by iodometric titration and from this the chromium (V) content of the sample was calculated. Attempts to determine total chromium contents directly by oxidation of the chromium (III), formed on disproportionation, to chromium (VI) using potassium bromate proved unsuccessful as the results obtained were rather erratic.

The lanthanide contents of the chromates (V) were determined gravimetrically by oxalate precipitation and subsequent ignition to oxides as described for lanthanum by Kolthoff and Elmquist (1931). In this method, samples of lanthanide chromates (V) were dissolved in 20 ml volumes of 2N hydrochloric acid, the solutions made 0.2N with respect to hydrochloric acid and heated to boiling. Oxalic acid solution was then added to give complete precipitation of the lanthanide ion and make the final solution 0.5N with respect to oxalic acid. This method gave satisfactory results for most of the lanthanide ions, but in the case of ytterbium, the oxalate appeared to have an appreciable solubility under these conditions. The analysis of this compound was carried out using the general recommendations for

lanthanide oxalate precipitations given by Broadhead and Heady (1960):-

(a) maintaining lanthanide ion concentrations above 0.01 M.

(b) using a 2- to 5- fold excess of oxalic acid.

(c) avoiding an excess of mineral acid - if possible maintaining the pH above 2.0.

(d) carrying out precipitation at room temperature and stirring the mixture for several minutes after precipitation.

This technique proved successful in reducing the solubility of the ytterbium oxalate.

The active oxygen contents of the lanthanide chromates (V) were determined by thermogravimetric analysis, experimental weight losses being compared with those predicted from the general equation:-

$$Ln\ CrO_4 \longrightarrow Ln\ CrO_3 + 0.5\ O_2$$

Complete analysis figures for the lanthanide chromates (V) are shown in Table I.

The lanthanide chromates (III) had previously been reported [Schneider et al. (1961) S. Quezel-Anbruncz and M. Mareschal (1963)] to have an orthorhombically distorted perovskite structure, space group O_{2h}^{16} - Pbnm. Using the reported cell dimensions, the dÅ spacings for these compounds were calculated from the appropriate equation given by D'Eye and Wait (1960) and conditions for reflection were obtained from the International Tables for Crystallography (1952). The experimental dÅ spacings were found to be in fairly good agreement with the calculated values, as shown in the Appendix - Tables AX to A XVII.

TABLE I

ANALYTICAL RESULTS FOR LANTHANIDE CHROMATES (V)

Compound	Cr(V) Content		Lanthanide Content		O Active		Ln: Cr: Oact.
	Calculated %	Experimental %	Calculated %	Experimental %	Calculated %	Experimental %	
Pr CrO_4	20.24	20.41	54.85	54.42	6.23	6.15	1: 1.02: 1
Gd CrO_4	19.03	18.96	57.55	57.32	5.86	5.91	1: 1: 1.01
Tb CrO_4	18.92	18.62	57.81	57.68	5.82	5.82	1.03: 1.02: 1
Dy CrO_4	18.67	18.66	58.35	58.40	5.74	5.80	1: 1: 1.01
Ho CrO_4	18.51	18.23	58.71	59.04	5.70	5.71	1: 1.02: 1.02
Er CrO_4	18.36	18.22	59.05	58.42	5.65	5.56	1.01: 1.02: 1
Yb CrO_4	17.99	17.76	59.87	58.92	5.54	5.57	1: 1: 1.02
Y CrO_4	25.38	25.08	43.39	43.50	7.81	7.68	1.02: 1: 1

Preparation, Characterisation and Thermal Decomposition of Praseodymium Chromate (VI)

The thermal decompositions of the chromates (VI) of lanthanum, samarium [Darrie (1967)] and neodymium [Kirkpatrick] have previously been investigated and shown to have two stages of decomposition in accordance with the equations:-

(a) $Ln_2 (CrO_4)_3 \rightarrow 2\ Ln\ CrO_4 + 0.5\ Cr_2O_3 + 1.25\ O_2$

(b) $2\ Ln\ CrO_4 \rightarrow 2\ Ln\ CrO_3 + 1.0\ O_2$

(c) $Ln_2 (CrO_4)_3 \rightarrow 2\ Ln\ CrO_3 + 0.5\ Cr_2O_3 + 2.25\ O_2$

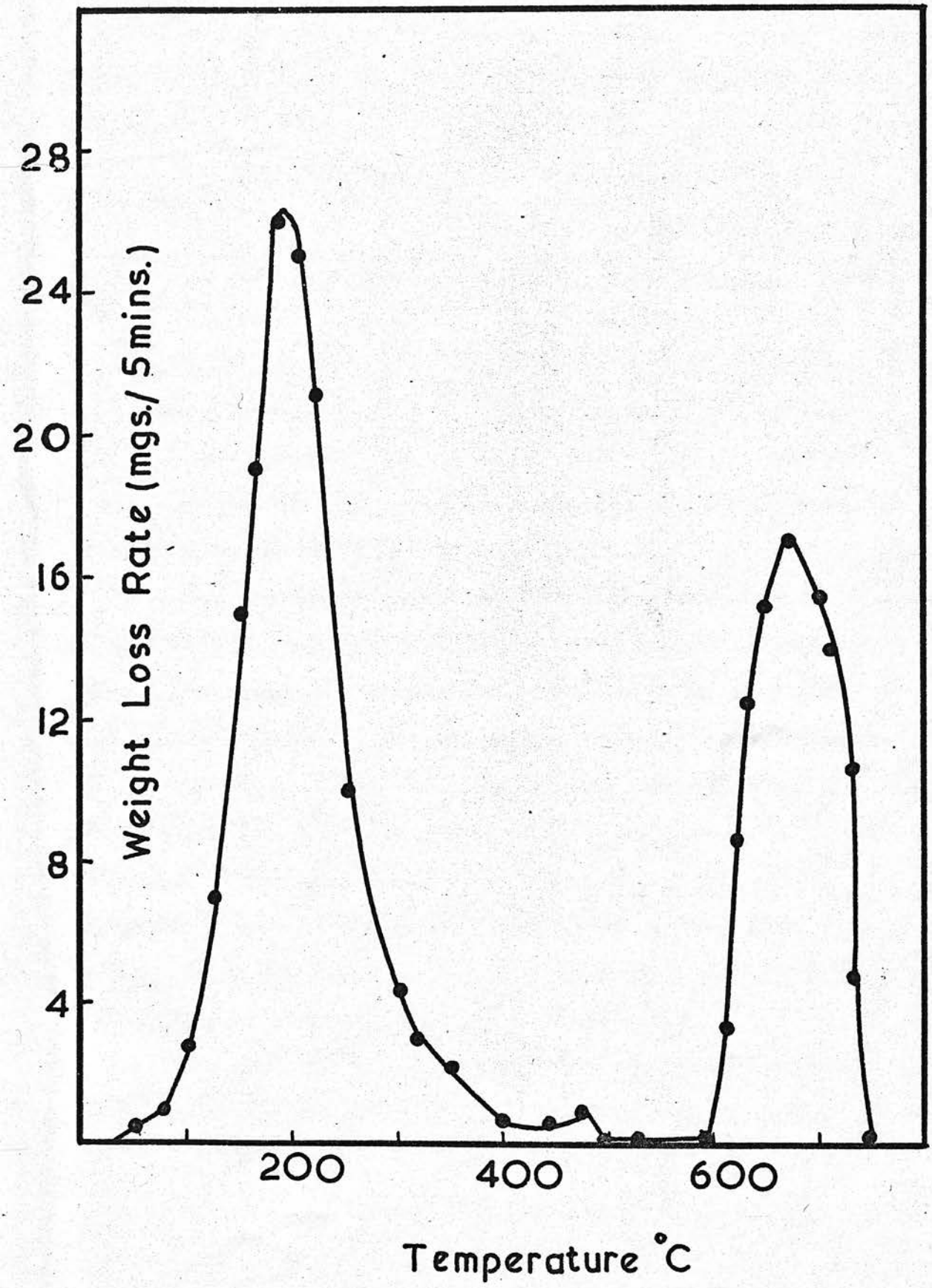
It has previously been reported [Schwarz (1963)] that the thermal decomposition of praseodymium chromate (VI) however showed only one stage of decomposition corresponding to equation (C) with no indication of the formation of a stable chromate (V) as an intermediate and this situation seemed to require re-examination.

Hydrated praseodymium chromate (VI) was prepared [Schwarz (1963)] by addition, at room temperature, of a 10% excess solution of aqueous sodium chromate to an aqueous solution of praseodymium nitrate and the resulting bright yellow precipitate dried in air at room temperature for several days. The chromium content of the product was determined by iodometric titration and the lanthanide ion by oxalate precipitation as described for the chromates (V). The degree of hydration was determined from the weight loss on heating the sample in air at 400°C for 48 hours. The analysis figures indicated the composition of the product to be $Pr_2 (CrO_4)_3 \cdot 7.5H_2O$.

Thermogravimetric analysis on hydrated $Pr_2 (CrO_4)_3$ showed [Fig. I] a single stage dehydration process, with maximum rate at 190°C, followed by a single stage chromate (VI) decomposition, with

FIG. I

T.G.A. CURVE FOR $Pr_2(CrO_4)_3$.Hydr.



maximum rate at 670°C. T.G.A. studies on anhydrous $Pr_2(CrO_4)_3$ confirmed this single stage chromate (VI) decomposition and experimental weight losses indicated that decomposition occurs according to:-

$$Pr_2(CrO_4)_3 \rightarrow 2\ PrCrO_3 + 0.5\ Cr_2O_3 + 2.25\ O_2$$

with no thermally stable chromate (V) intermediate. Partially decomposed samples of anhydrous $Pr_2(CrO_4)_3$ were examined by X-ray powder diffraction and later by electron spin resonance in an attempt to identify chromate (V) since it was assumed that although thermally unstable, it must still be formed in the course of the decomposition. The results of these investigations will be discussed later.

As indicated previously, praseodymium alone among the lanthanide ions used presented difficulties in the preparation of the chromate (V) compound. Preliminary preparations using as starting material the oxide Pr_6O_{11} gave products which from analysis and X-ray diffraction appeared to be quite satisfactory, but which T.G.A. runs showed to decompose in two stages [Fig. II], the relative weight losses of which varied with small changes in reaction conditions. The preparation was then repeated using as starting material, Pr_2O_3 - obtained by hydrogen reduction of Pr_6O_{11} at 660°C. The product obtained initially was shown by T.G.A. to have a small chromate (VI) impurity, but heating in air at 600°C succeeded in decomposing this impurity to chromate (V) leaving the compound in a state of high purity [Fig. III].

Thermal Analysis of Chromates (V)

The course of the thermal decompositions of the chromates (V) of Pr, Gd, Tb, Dy, Ho, Er, Yb and Y were followed using the Stanton Massflow thermobalance. 1.00grm. samples of the chromates (V) were heated in air from room temperature to 1100°C at a rate of 6°C per

FIG. II

T.G.A. CURVES FOR $PrCrO_4$ (1st. Attempts)

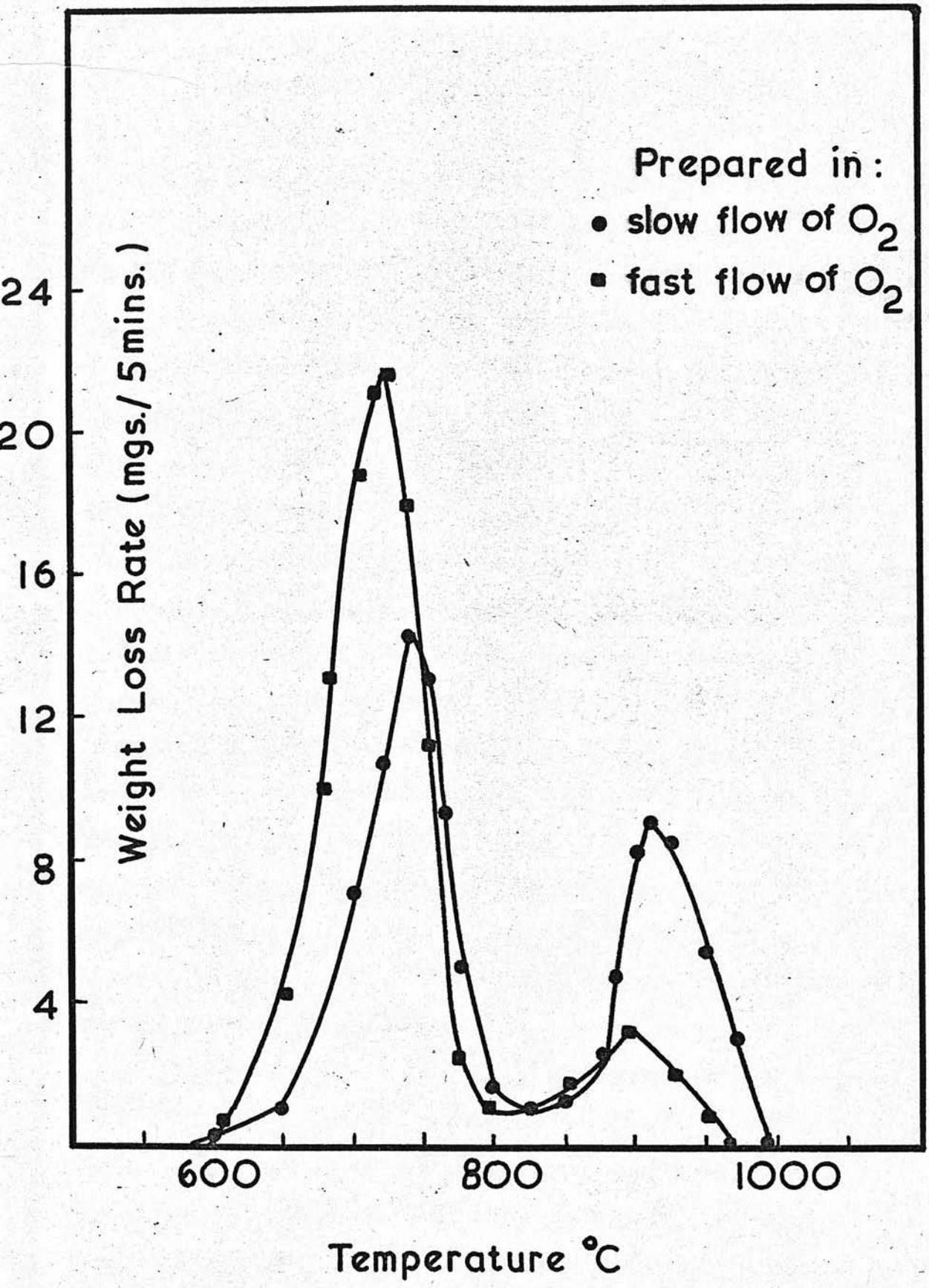
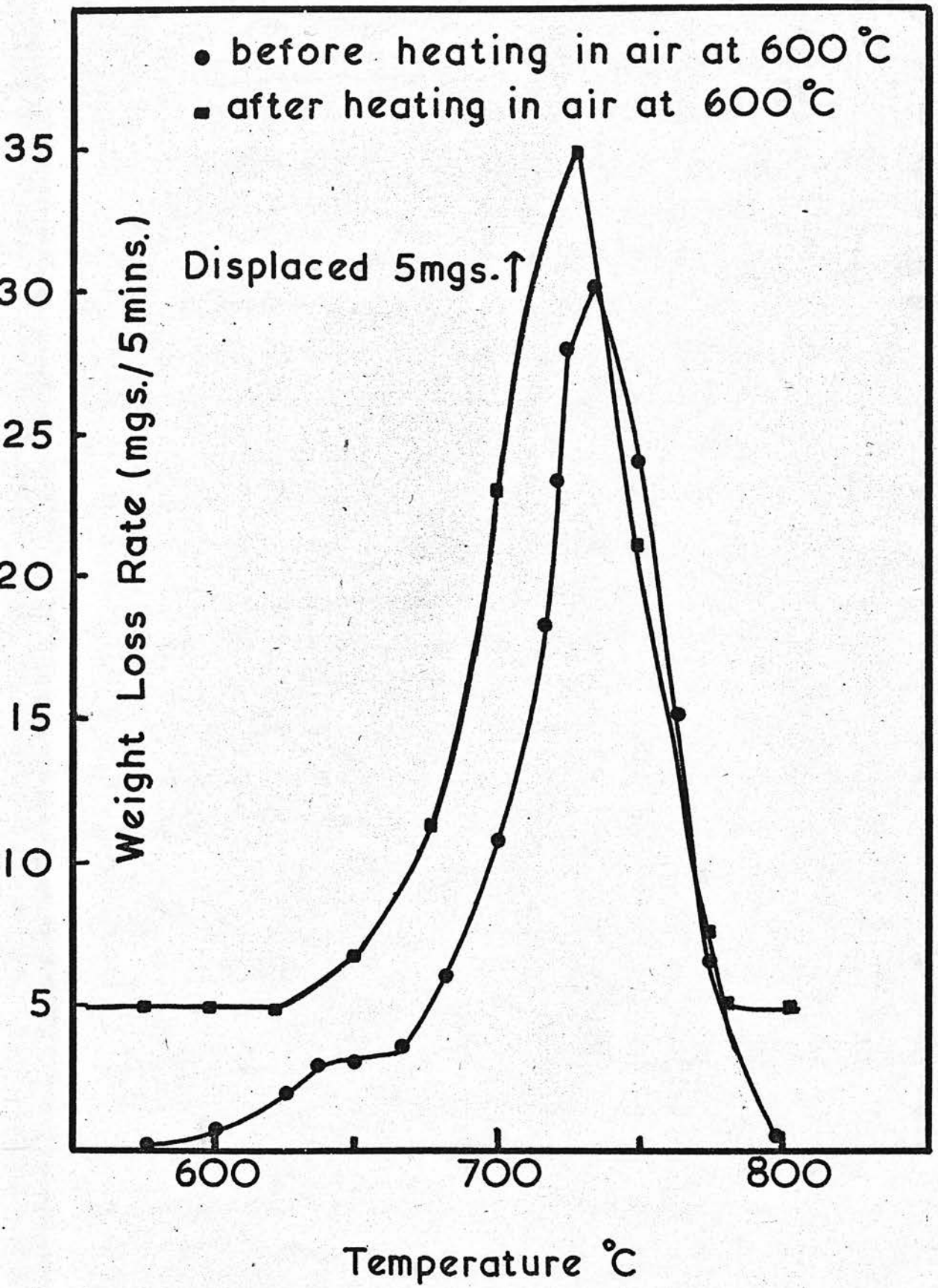


FIG. III

T.G.A. CURVES FOR $PrCrO_4$



minute. Differential curves, plotting weight loss per 5 minute interval against temperature, showed each of these compounds to have a single-stage decomposition, in accordance with the equation:-

$$Ln\ CrO_4 \rightarrow Ln\ CrO_3 + 0.5\ O_2$$

A typical example of these differential plots is shown for Er CrO_4 in Fig. IV.

Differential Thermal Analysis (D.T.A.) of some of these lanthanide chromates (V) showed as the main feature a medium endotherm around 730°C and a typical run is shown, for Er CrO_4, in Fig. V. Differential thermal analysis results for the chromates (V) of lanthanum, neodymium and samarium have previously been reported [Darrie (1967)] and these are shown with the results from the present work in Table II. The good agreement found between D.T.A. and T.G.A. results [Table III] show that the endothermic feature found from D.T.A. corresponds to the decomposition of the lanthanide chromate (V).

TABLE II

TEMPERATURES (°C) OF THE D.T.A. ENDOTHERMS OF CHROMATES (V)

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y
From	705		629	650		705				679	692	689		675	702
Maximum	765		735	715		740				725	725	733		727	752
To	820		762	780		810				857	826	831		800	861
Change of Slope										774	774				800

FIG. IV

T.G.A. CURVE FOR $ErCrO_4$

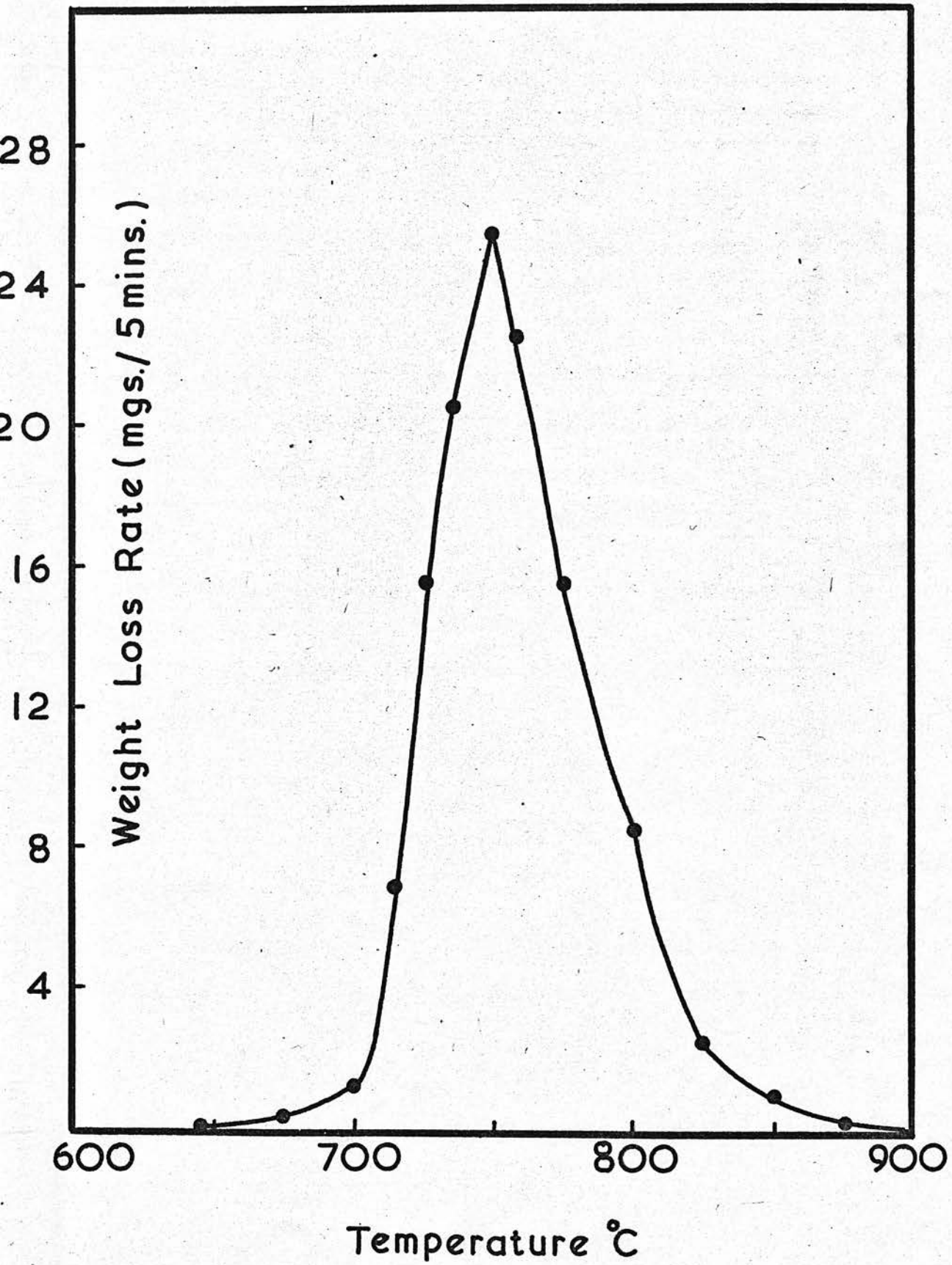


FIG. V

D.T.A. CURVE FOR $ErCrO_4$

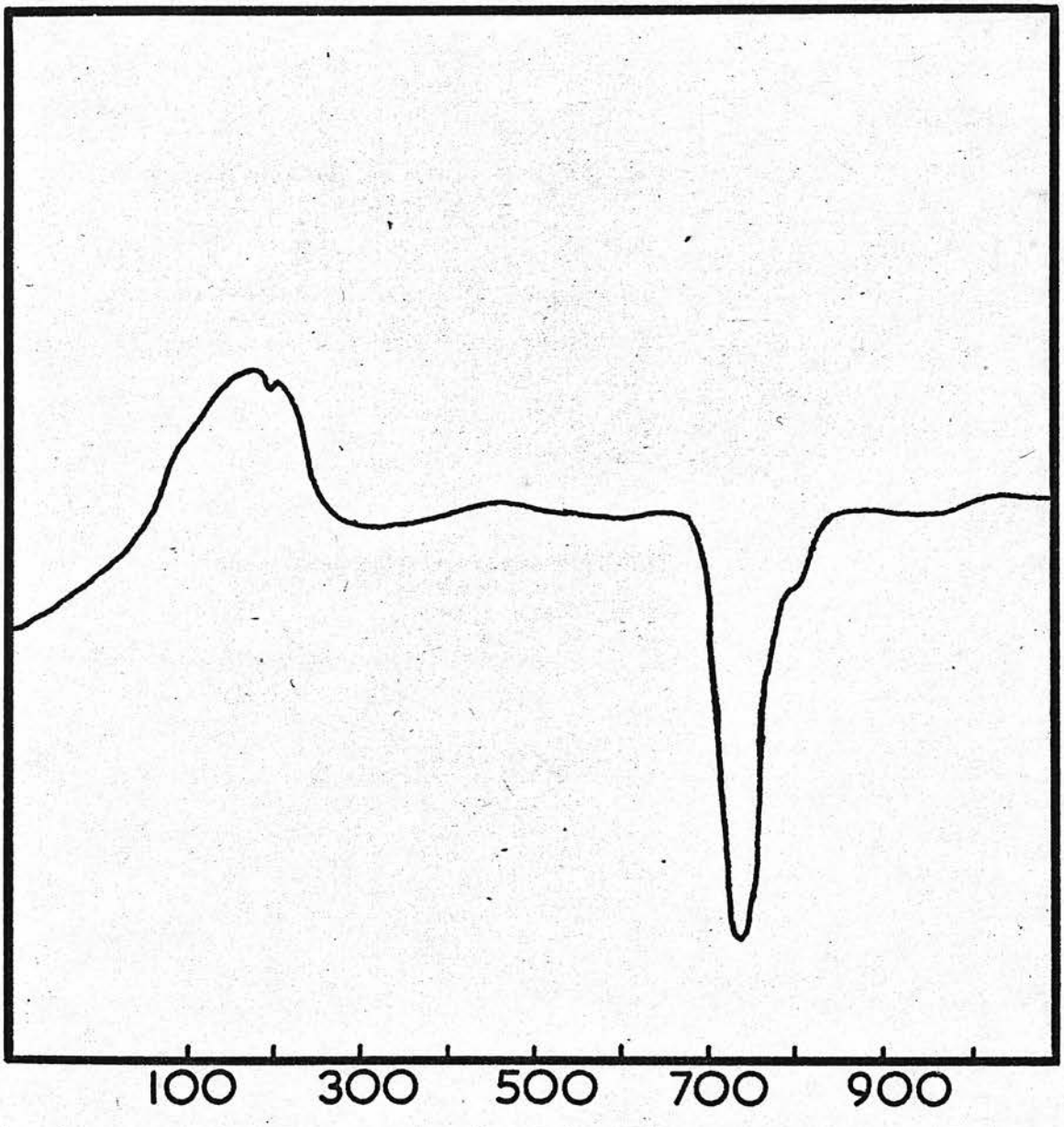


TABLE III

COMPARISON OF D.T.A. AND T.G.A. DECOMPOSITION

TEMPERATURES (°C) FOR CHROMATES (V)

	Pr		Gd		Tb		Dy		Ho		Er		Yb		Y	
	D.T.A.	T.G.A.	D.T.A.	T.G.A.	D.T.A.	T.G.A.	D.T.A.	T.G.A.	D.T.A.	T.G.A.	D.T.A.	T.G.A.	D.T.A.	T.G.A.	D.T.A.	T.G.A.
From	629	620	Not Known	675	Not Known	675	679	685	692	685	689	690	675	675	702	710
Maximum	735	725		760		735	725	735	725	740	733	745	727	732	752	762
To	762	785		900		860	857	850	826	870	831	850	800	800	861	860
Change of Slope						765	774	755	774	780					800	800

The formation of chromates (III) from reaction of chromium (III) oxide with lanthanide oxide was also examined by differential thermal analysis. The thermal features of chromium (III) oxide and some of the lanthanide oxides were determined by carrying out D.T.A. runs on these compounds above. Stoicheiometric mixtures of chromium (III) oxide with a lanthanide oxide were then studied by D.T.A. and X-ray diffraction data used to show that reaction had occurred during the run. Reaction of the two oxides was found to be represented by a small exothermic feature in each case with temperatures of reaction as shown in Table IV.

TABLE IV

REACTION TEMPERATURES OF Ln_2O_3/Cr_2O_3 MIXTURES

Lanthanide Ion	Pr^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Yb^{3+}	Y^{3+}
Temperature of exotherm (°C)	714	756 725	690	714	747	756

X-Ray Diffraction Work on Chromates (V) and Praseodymium Chromate (VI)

X-ray powder diffraction patterns were recorded for hydrated and anhydrous praseodymium chromate (VI) and the chromates (V) and where possible, the measured dÅ spacings compared with previously reported values. No previous information is available on the crystal structure of hydrated or anhydrous praseodymium chromate (VI) but experimental dÅ spacing shown in Table A IX bear a close relationship to those preveiously reported for the hydrated and anhydrous chromates VI of lanthanum and samarium [Darrie (1967)].

The dÅ spacings of the chromates (V) studied are shown in Table A I to A VIII of the appendix. Praseodymium chromate (V) has been reported [Schwarz (1963)] to have a mixed zircon and Huttonite structure; and by Bertaut et al. (1964), a pure zircon structure. No previously reported dÅ spacings are available in the literature but measurements made from a diffraction pattern shown by Schwarz (1963) and values calculated from cell dimensions given by Bertaut et al. (1964) are shown in Table A I.

Experimental measurements indicate that Pr CrO_4 does indeed show reflections corresponding to a mixture of Zirconite and Huttonite structures.

The remainder of the chromates (V) studied, have been reported [Schwarz (1963); Bertaut et al. (1964)] as having the tetragonal zircon structure, with space group $I4_1/amd$ - D_{4h}^{19}. Using the given cell dimensions and known conditions for reflection, applied to the formula for a tetragonal system given by D'Eye and Wait (1960) $\left[d = \frac{ac}{\sqrt{(h^2 + k^2)\, c^2 + l^2 a^2}} \right]$, values for the dÅ spacings of the chromates(V) studied were calculated and found to be in good agreement with experimental values.

Ultraviolet and Visible Spectra of chromates V, chromates III, and praseodymium chromate VI

The ultraviolet and visible diffuse reflectance spectra of hydrated and anhydrous $Pr_2(CrO_4)_3$ [Fig. VI], the chromates (V) [Fig. VII] and the chromates (III) [Fig. VIII] were measured. The absorption maxima of these spectra will be quoted and discussed later. No previous values have been quoted in the literature for the absorption maxima of praseodymium chromate (VI), or for any of the chromates (V) studied. Comparisons will however be made with values quoted for other lanthanide chromates (VI) and (V) [Darrie (1967); Darrie, Doyle and Kirkpatrick (1966)]. Of the chromates (III) studied, previously reported values are available for yttrium chromate (III) [Reinen and Schmitz - Dumont (1959)] but again comparisons may be made with the values quoted by Darrie et al. (1966) for the chromates (III) at lanthanum, samarium and neodymium.

Infrared Absorption Spectra of Chromates (V), Chromates III and Praseodymium Chromate VI

The infrared absorption spectra of these compounds were measured using both potassium bromide disk and Nujol mull techniques and some spectra are reproduced in Figs. IX and X. The absorption maxima of the chromates V and III are shown in tables V and VI respectively and a comparison of absorption maxima of hydrated and anhydrous praseodymium chromate with previously recorded values for lanthanum, samarium and neodymium [Darrie, Doyle and Kirkpatrick (1967)] is shown in Table VII.

FIG. VI

DIFFUSE REFLECTANCE SPECTRA OF $Pr_2(CrO_4)_3 \cdot Hydr.$ AND $Pr_2(CrO_4)_3$

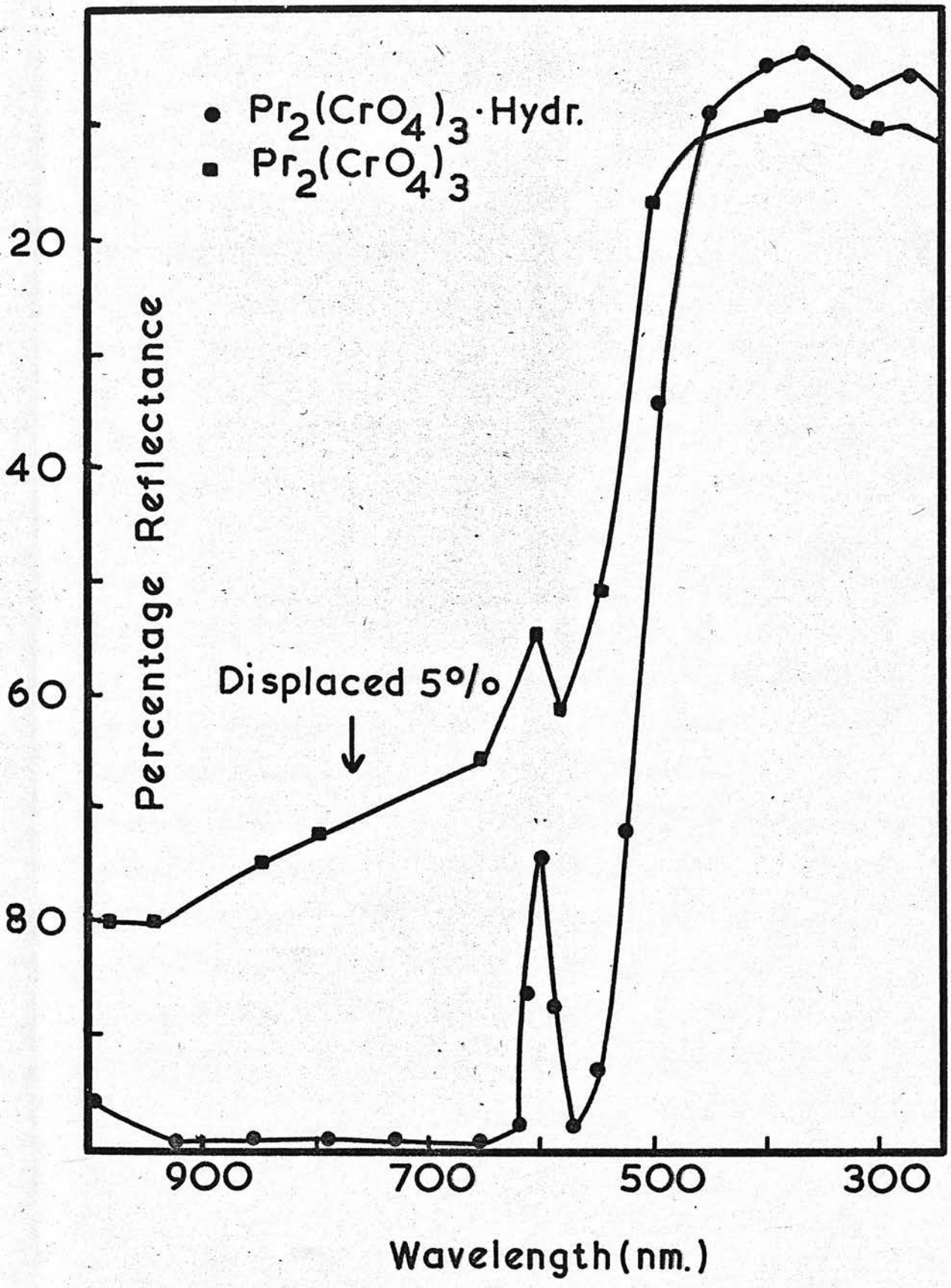


FIG. VII

DIFFUSE REFLECTANCE SPECTRA OF SOME CHROMATES(V)

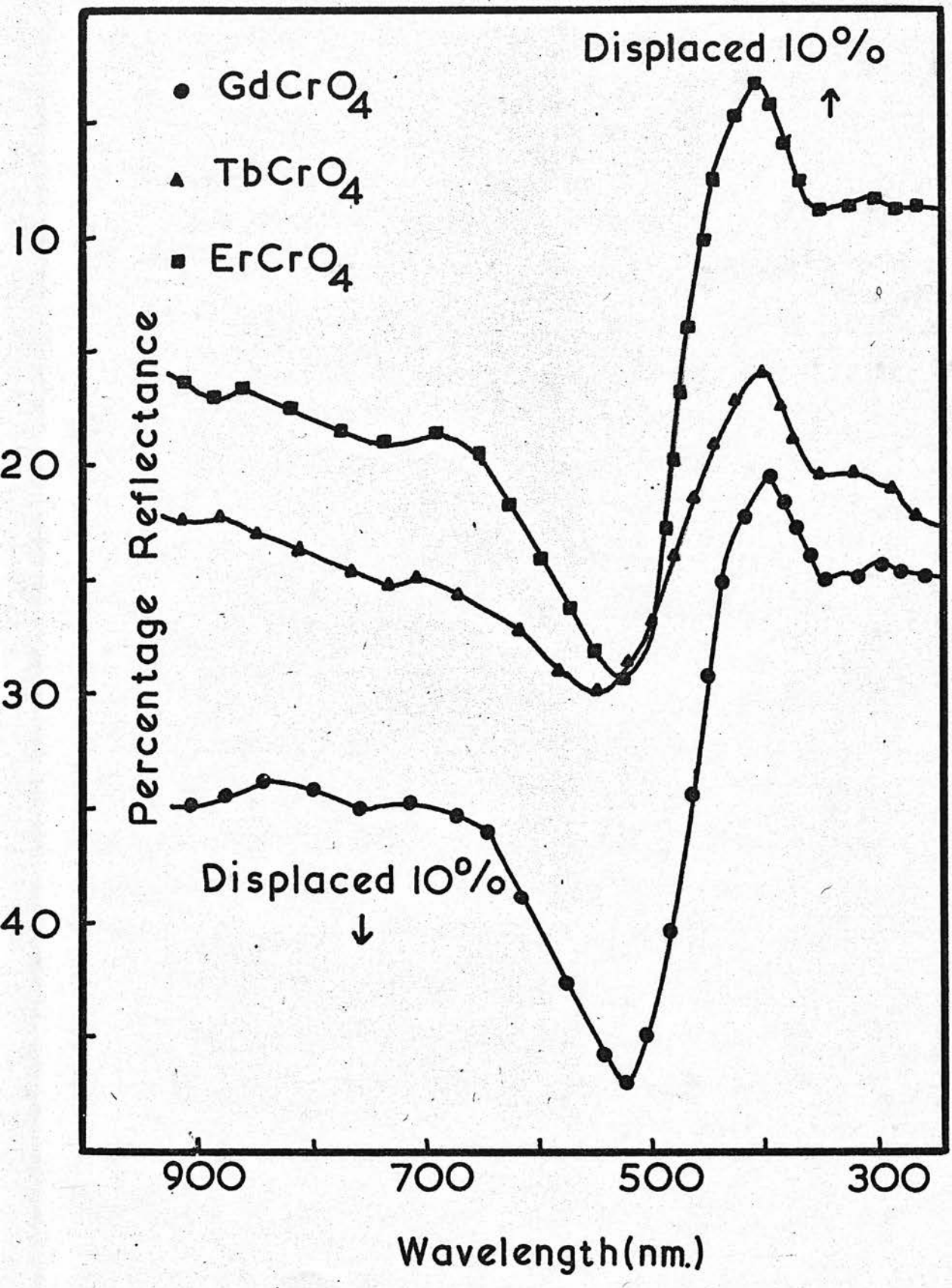


FIG. VIII

DIFFUSE REFLECTANCE SPECTRA OF SOME CHROMATES(III)

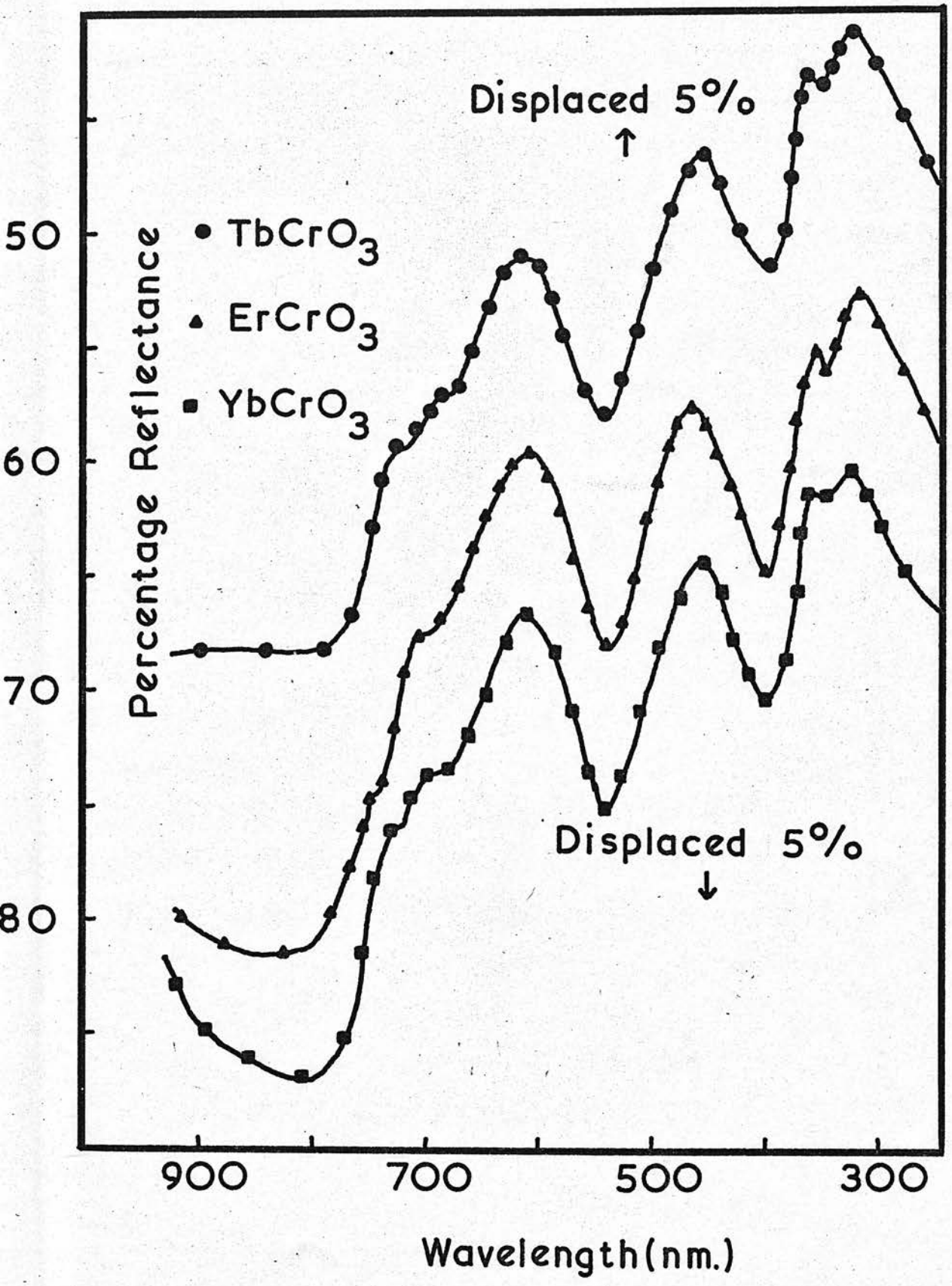


TABLE V

I.R. ABSORPTION SPECTRA OF CHROMATES (V)

Observed, Maxima (cm^{-1})

$PrCrO_4$		$GdCrO_4$		$TbCrO_4$		$DyCrO_4$		$HoCrO_4$		$ErCrO_4$		$YbCrO_4$		$YCrO_4$	
K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull
			971 w.sh.												
		943 w.	948 w.		950 w.	950 w.sh.	940 w.sh.								
			916 w.sh.												
			888 w.sh.		888 w.sh.										
		861 w.	867 w.sh.	866 w.sh.	868 w.sh.	860 w.sh.	860 w.sh.								
838 w.sh.	844 w.sh.	838 w.	841 w.sh.	838 w.sh.				835 w.sh.	843 w.sh.	836 w.sh.	842 w.sh.	859 w.sh.	852 w.sh.	850 w.sh.	843 w.sh.
788 m.br.	792 m.br.	770 s.	768 s.	779 s.	773 s.	777 s.	ca. 760	780 s.	772 s.	780 s.	772 s.	783 s.	780 s.	780 s.	776 s.
732 s.	ca. 730														

w. = weak
m. = medium
s. = strong
sh. = shoulder
br. = broad
v.br. = very broad

The Nujol Mull spectra of some of these chromates (V) were difficult to interpret due to the presence of the Nujol absorption maximum at 725 cm-1

FIG. IX

I.R. ABSORPTION SPECTRA OF SOME CHROMATES(V)

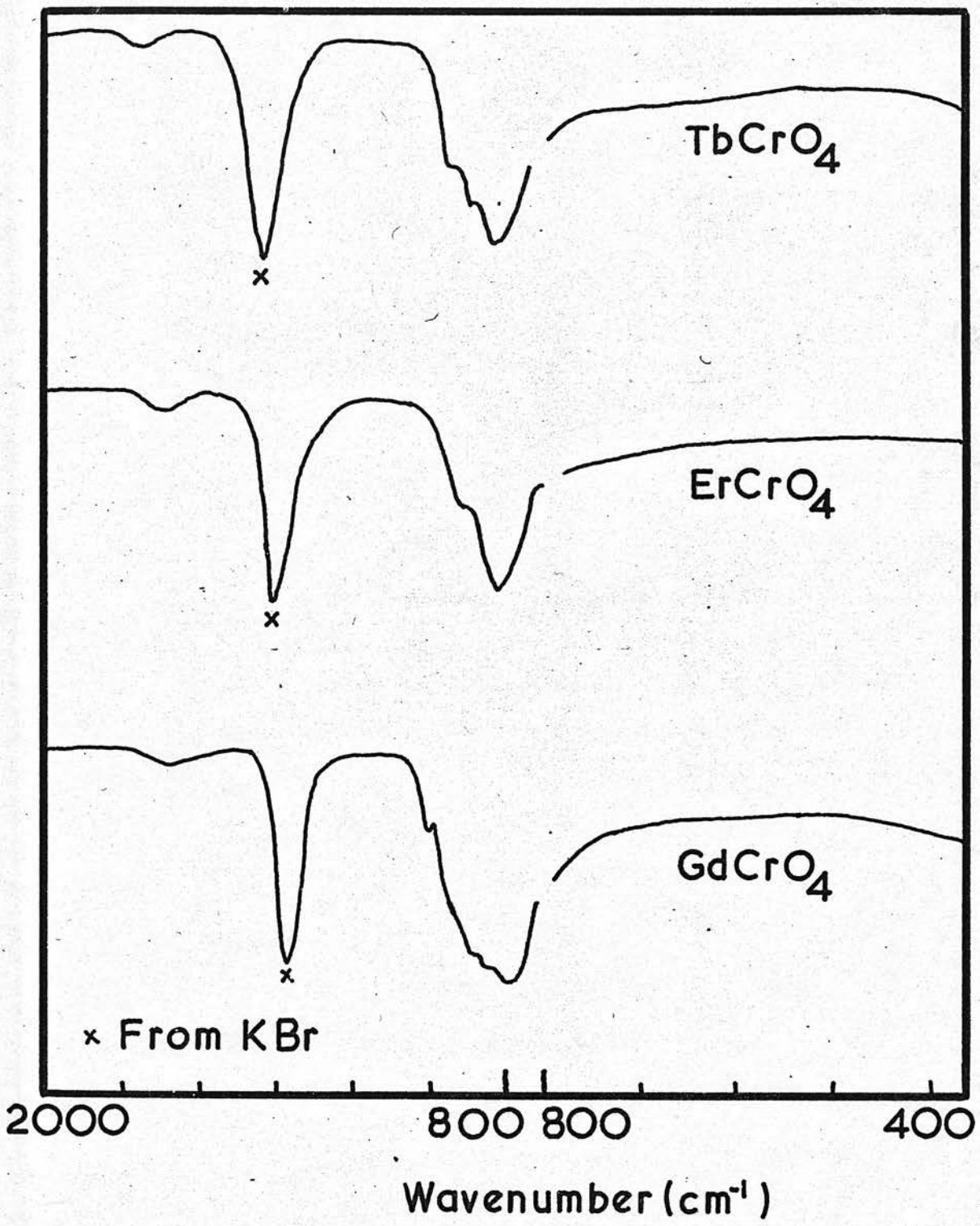


TABLE VI

I.R. ABSORPTION SPECTRA OF CHROMATES (III)

OBSERVED MAXIMA, (cm^{-1})															
Pr CrO_3		Gd CrO_3		Tb CrO_3		Dy CrO_3		Ho CrO_3		Er CrO_3		Yb CrO_3		Y CrO_3	
K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull	K Br disk	Nujol Mull
610 v.br.	619 s.br.			611 m.br.	ca610 m.br.	612 s.br.	610 m.br.	620 m.br.	617 m.br.	608 m.br.	608			619 s.br.	610 s.br.
	598 s.br.	585 s.vbr.	580 s.vbr.	586 s.br.	585 s.br.	580 s.vbr.	582 s.vbr.	584 s.br.	585 s.br.	584 s.br.	583 s.br.	588 v.br.	592 v.br.	588 s.br.	585 s.br.
				568 w.sh.	565 w.sh.	568 w.sh.	570 w.sh.	570 w.sh.	565 w.sh.	572 w.sh.	570 w.sh.	575 m.sh.	575 m.sh.	565 w.sh.	570 w.sh.
				521 w.	519 w.	525 w.	523 w.	526 w.	530 w.	532 w.sh.	533 w.sh.			532 m.	531 m.
		513 m.br.	510 m.br.					510 w.						510 m.	510 m.
488 m.sh.	492 m.sh.	480 m.br.	480 m.br.	487 m.br.	485 m.br.	483m. v.br.	486 m.br.	492 m.br.	492 m.br.	496 m.br.	490 m.br.	502 m.br.	500 m.br.	492 s.	493 s.
457m.	455m.														
423 m.	425 m.			443 m.	440 m.	442 m.	440 m.	435 m.br.	435 m.br.	438 m.	435 m.	442 m.br.	442 m.br.	442 m.	441 m.

w = weak, m = medium, s = strong

sh = shoulder, br = broad, v.br = very broad

FIG. X

I.R. ABSORPTION SPECTRA OF SOME CHROMATES(III)

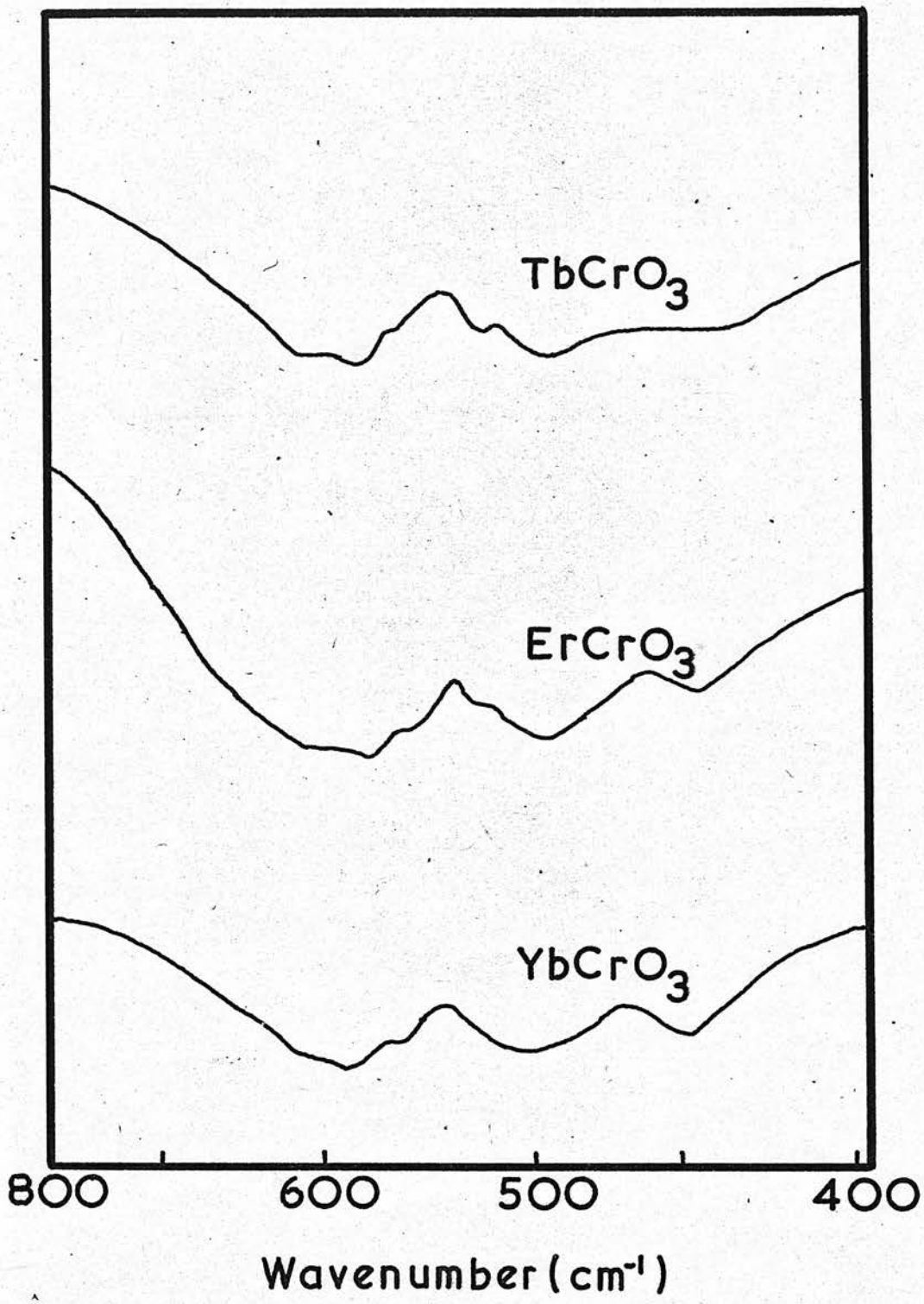


TABLE VII

COMPARISON OF I.R. SPECTRUM OF PRASEODYMIUM CHROMATE (VI)

WITH OTHER LANTHANIDE CHROMATES VI

OBSERVED MAXIMA (cm^{-1})

$La_2(CrO_4)_3$.Hydr.*	$Nd_2(CrO_4)_3$.Hydr.*	$Sm_2(CrO_4)_3$.Hydr.*	$Pr_2(CrO_4)_3$.Hydr.	$La_2(CrO_4)_3$*	$Nd_2(CrO_4)_3$*	$Sm_2(CrO_4)_3$*	$Pr_2(CrO_4)_3$
1640 s.br.	1640 m.br.	1630 m.br.	1630 m.br.				
						1000 w.sh.	1005 m.
945 w.		945 m.sh.		930 w.sh.	935 s.br.	935 s.	940 s.
915 s.	910 s.br.	920 s.br.	920 s.br.	920 s.			
895 s.		900 w.sh.		900 w.sh.		900 m.sh.	
860 m.	865 m.	865 m.	865 m.			865 w.sh.	860 m.
840 m.	845 m.	845 w.	850 m.				
820 m.	820 m.	820 w.	825 m.				
				775 s.br.	780 s.br.	775 s.br.	790 s.br.
630 m.br.	635 m.br.	630 w.br.	625 w.br.				
					455 m.	455 m.sp.	455 m.
432 m.	433 m.	430 m.			435 m.	432 m.sp.	435 m.

w = weak
b = broad
m = medium
s = strong
sh = shoulder
sp = sharp

* Reference:- Darrie, Doyle and Kirkpatrick (1966)

MAGNETIC MEASUREMENTS ON CHROMATES (V), CHROMATES (III) AND PRASEODYMIUM CHROMATE (VI)

Room temperature magnetic susceptibilities of these compounds were measured, using the Gouy method and values for effective magnetic moments (μ_{eff}) were calculated. The results are shown in Tables VII and VIII.

TABLE VIII

MAGNETIC DATA FOR CHROMATES V AND PRASEODYMIUM CHROMATE VI

Compound	Susceptibility/gm. ($10^6 \times \chi$)	Magnetic Moment (μ_{eff}) B.M.	Temperature ($^{\circ}C$)
$Pr_2(CrO_4)_3$.Hydr.	13.78	3.56	19.3
$Pr_2(CrO_4)_3$	16.84	3.55	19.0
$PrCrO_4$	23.96	3.81	19.0
$GdCrO_4$	100.66	8.02	16.9
$TbCrO_4$	149.80	9.85	19.2
$DyCrO_4$	173.03	10.64	18.1
$HoCrO_4$	164.10	10.38	16.8
$ErCrO_4$	137.11	9.51	16.1
$YbCrO_4$	30.98	4.62	21.7
$YCrO_4$	6.07	1.70	16.6

TABLE VIX

MAGNETIC DATA FOR CHROMATES (III)

Compound	Grm. Susceptibility ($10^6 \times \chi$)	Magnetic Moment (μ eff)	Temperature ($^{\circ}C$)
Pr CrO_3	31.52	4.22	17.5
Gd CrO_3	97.42	7.65	16.1
Tb CrO_3	132.56	9.03	21.5
Dy CrO_3	153.47	9.73	18.3
Ho CrO_3	149.33	9.60	15.7
Er CrO_3	128.27	8.96	17.4
Yb CrO_3	36.75	4.85	17.5
Y CrO_3	16.65	2.71	15.5

RESULTS FROM ELECTRON-SPIN RESONANCE STUDIES

It has been stated previously in the text that some electron-spin resonance e.s.r. studies were carried out on the praseodymium chromate (VI), (V) and (III) system and some of the background work for this is described below.

Before attempting studies on the praseodymium compounds, it was necessary to investigate the techniques involved in recording e.s.r. spectra and to examine the capabilities of the instrument, the Hilger and Watts Microspin E.S.R. 5., with regard to accuracy and reproducibility of results. Since this investigation was the first to be done using this instrument and no previous work on e.s.r. spectroscopy had been performed in this department, this preliminary investigation was required to be fairly comprehensive. The initial work therefore was restricted to compounds for which results were available from the literature and which best demonstrated phenomena such as hyperfine

splitting and zero-field splitting. Examinations were carried out to demonstrate the types of spectra obtained from samples in solution as glasses and in polycrystalline form. The effects of diamagnetic dilution and reduction of temperature on spectral line widths were also investigated.

The compound chosen to provide an example of nuclear hyperfine splitting was vanadyl acetylacetonate in which vanadium has electron spin of $\frac{1}{2}$ and only the nuclear spin of vanadium [$I = 7/2$] influences the spectrum [Wilson and Kivelson (1966)]. A solution of vanadyl acetylacetonate in de-gassed toluene [approx. 2.5×10^{-3} M] was prepared and the spectrum recorded at room temperature. The spectrum consisted of eight hyperfine lines (corresponding to $2I + 1$ lines) with a separation between first and last of approximately 700 Gauss. Measurement of splitting between neighbouring peaks showed that this value was not constant but increased from low field to high field. Since the separation of the hyperfine peaks was not constant, calculation of a_o - the hyperfine splitting constant, and g_o - the spectroscopic splitting factor, required simultaneous solution of the second order equations:-

$$(a)\quad a_o = -g_o \beta_o (H_M - H_{-M}) \,/\, 2M\hbar$$

$$(b)\quad g_o - g_s = g_s \left(\frac{H_s - \frac{1}{2}(H_M + H_{-M})}{\frac{1}{2}(H_M + H_{-M})} \right) - \frac{2a_o^2 \hbar \left[I(I+1) - M^2\right]}{g_s \beta_o^2 (H_M + H_{-M})^2}$$

where:- g_s is the g-value of some standard - in this case diphenyl picryl hydrazyl (D.P.P.H)

H denotes magnetic field value

I the nuclear spin number

M the quantum number defining the component of angular momentum along the applied magnetic field.

The values obtained in this work were as follows:-

$$a_o = (9.71 \pm 0.11) \times 10^{-3} \text{ cm}^{-1}$$

$$g_o = 1.944 \pm 0.021$$

these compare quite well with the values in the literature [Wilson and Kivelson (1966)] :-

$$a_o = 9.82 \times 10^{-3} \text{ cm}^{-1} \; ; \; g_o = 1.969$$

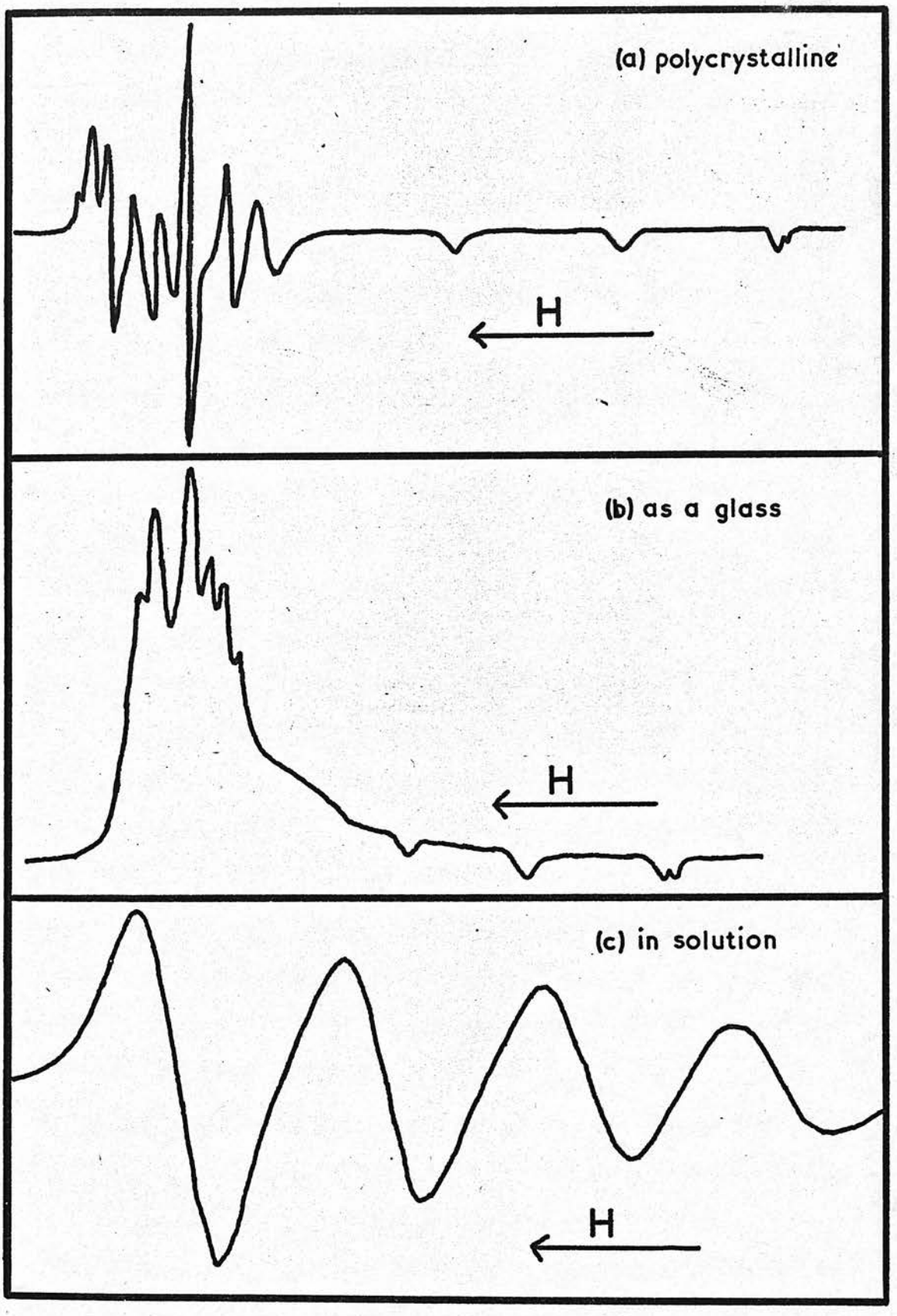
A study of the electron-spin resonance spectrum of copper (II) acetylacetonate proved useful in providing a fairly comprehensive coverage of the techniques involved in e.s.r. spectroscopy. This compound was examined in solution, as a glass [Gersmann and Swalen (1962)] and in a diamagnetically diluted polycrystalline form, and results from the different phases compared. When in the form of a glass, or in crystalline form, copper (11) acetylacetonate is anisotropic and so gives a different g-value and splitting constant for the orientation where the applied magnetic field is parallel to the crystalline axis and where the magnetic field is perpendicular to the crystalline axis. When a compound such as this is studied in solution, the tumbling motion of the molecules gives rise to a resultant spectrum giving only one g-value and one hyperfine splitting constant.

The spectrum of copper (11) acetylacetonate in solution [approx. 7×10^{-3} M with a 60% toluene - 40% chloroform mixture as solvent] was recorded and showed four hyperfine lines [Fig. X1] as expected for the nuclear spin number of copper, $I = 3/2$. The solution was then frozen in liquid nitrogen to form a glass and the spectrum again recorded, but now showing a more complex system of lines [Fig. X1] as due to the molecules now having been fixed in their orientation, the anisotropy becomes apparent.

When examining the e.s.r. spectrum of a polycrystalline sample, it is necessary, for good resolution, to try to counteract the two

FIG. XI

E.S.R. SPECTRUM OF Cu(II) ACETYLACETONATE



major causes of line-broadening. These are:- (a) spin-lattice interactions. (b) spin-spin interactions. The effect of spin-lattice interactions may be reduced simply by cooling the sample while spin-spin interactions, due to the close proximity of the paramagnetic ions, may be reduced by incorporating the paramagnetic compound, in low concentration, into the lattice of an isomorphous diamagnetic compound.

It has been reported [Maki and McGarvey (1958)] that a suitable diluent for copper (11) acetylacetonate is the isomorphous palladium (11) acetylacetonate and that satisfactory spectra result from polycrystalline samples of palladium (11) acetylacetonate containing 0.5 mole % of copper (11). A sample of diluted crystals was prepared by slow crystallisation from a chloroform solution containing the desired proportions of palladium (11) acetylacetonate and copper (11) acetylacetonate. The resulting crystals were ground up, so as to be polycrystalline and gave a satisfactory spectrum at room temperature [Fig. X1]. The equations used in the calculations for the glass and polycrystalline spectra were those given by Ingram (1955) and a comparison of results is shown in Table IX.

TABLE X

RESULTS FROM E.S.R. STUDIES ON COPPER (11) ACETYLACETONATE

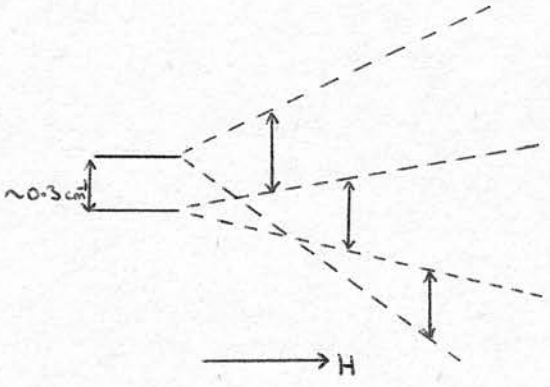
	OBSERVED						LITERATURE					
Nature of Sample	$g_{//}$	$g_{\perp}$	$A_{//}$ (cm^{-1})	$A_{\perp}$ (cm^{-1})	g_o	A_o (cm^{-1})	$g_{//}$	$g_{\perp}$	$A_{//}$ (cm^{-1})	$A_{\perp}$ (cm^{-1})	g_o	A_o (cm^{-1})
In solution	-	-	-	-	2.08	-75×10^{-4}	-	-	-	-	2.112	-67.8×10^{-4} (a)
As a glass	2.278	2.038	-180.5×10^{-4}	-30.2×10^{-4}	2.12	-80.3×10^{-4}	2.264	2.036	-145.5×10^{-4}	-29.0×10^{-4}	2.112	-67.8×10^{-4} (a)
In polycrystalline form	2.266	2.054	-183.6×10^{-4}	-24.5×10^{-4}	2.125	-77.5×10^{-4}	2.266	2.054	-160×10^{-4}	-19.5×10^{-4}	2.125	-66.3×10^{-4} (b)

References:- (a) Gersmann and Swalen (1962)

(b) Maki and McGarvey (1958)

Agreement between observed and literature g-valves is good, but there are significant differences between observed and experimental values for splitting constants.

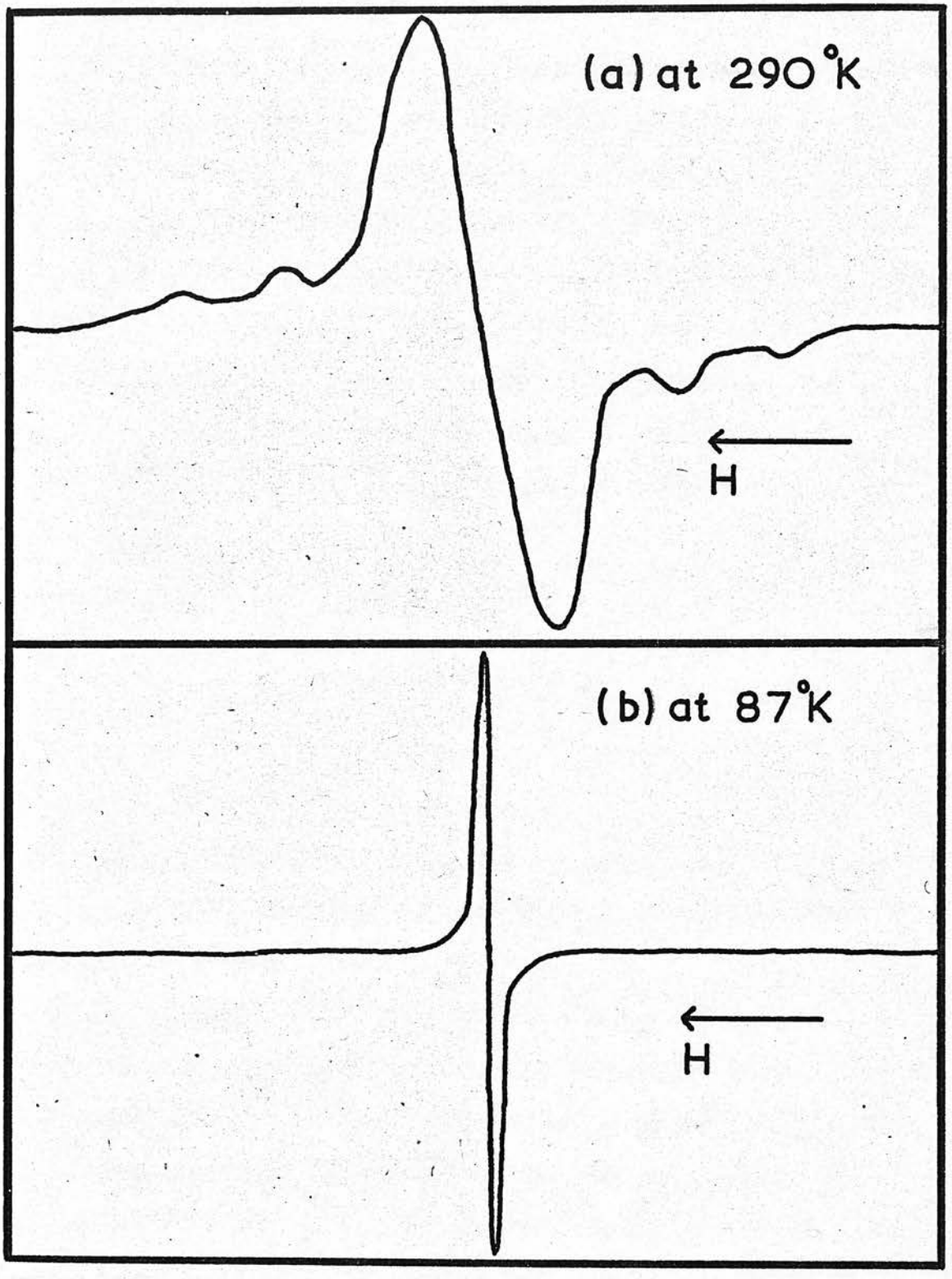
It has been reported previously [Bagguley and Griffiths (1947)], that in crystalline environment, the chromium (111) ion shows the phenomenum known as zero-field splitting. The chromium (111) ion, ground state ^4F, has an orbital singlet lying lowest, approximately 10^4 cm^{-1} below the first triplet when in an environment of cubic symmetry; chromium (111) has three electrons in the 3d shell giving a spin degeneracy of 4. The orbital singlet is split by a field of lower symmetry to form two doublets with a separation of about 0.3 cm^{-1} [Bleaney et al. (1951)]. These doublets are not split further by the crystalline field as an electric field will always leave a system containing an odd number of electrons with an even degeneracy [Kramers (1930)]. Application of an external magnetic field splits these doublets and transitions between the levels are observed as shown below.



The compound chosen for study was the hydrated ammonium chromium sulphate, $NH_4\ Cr(SO_4)_2\ .12H_2O$ which had previously been investigated [Burns (1961)], using the isomorphous ammonium aluminium sulphate, $NH_4Al\ (SO_4)_2\ .12H_2O$ as diluent. A diluted sample was prepared by crystallisation from an aqueous solution of the aluminium salt containing 1 mole per cent of the chromium salt. The room temperature e.s.r. spectrum of this sample, shown in Fig. X11, was used to calculate the anisotropic g-values and D, the electronic splitting coefficient, for the chromium (111) ion. The values found

FIG. XII

E.S.R. SPECTRUM OF CHROMIUM(III) (1%) IN $NH_4Al(SO_4)_2 \cdot 12H_2O$



for this compound, which differ slightly from previously reported values, were as follows:-

$g_{//} = 1.9743$; $g_{\perp} = 1.9736$; $D_{//} = 0.0366\ cm^{-1}$; $D_{\perp} = 0.0399\ cm^{-1}$

Lit.:- $g_{//} = 1.977$; $g_{\perp} = 1.978$; $D_{//} = 0.0489\ cm^{-1}$; $D_{\perp} = 0.0492\ cm^{-1}$

Reference:- Burns (1961)

When examined at liquid nitrogen temperature (-186°C), the line-width of the spectrum of this compound was greatly reduced and showed only the main central band [Fig. XII]. This effect was previously observed by Bleaney (1950) who reported that the splitting diminishes by approximately 0.5 cm^{-1} per 100°K fall in temperature, becoming so small that no resolved side-peaks can be observed at 90°K.

Studies by E.S.R. on chromium oxidation states in praseodymium chromates (VI), (V), and (III) proved to be rather unsuccessful. The E.S.R. spectrum of chromium (V) in the CrO_4^{3-} ion had previously been recorded, with the sample in the form of an alkaline glass, [Carrington et al. (1956)] and found to consist of a single line which could be observed only at 20°K. The line shape was assymetrical with a prominent shoulder on the side of the peak which was interpreted as indicating a g-value variation [$g_{//} = 1.98$; $g_{\perp} = 1.97$]. In the present work, in which an attempt was made to prove, by E.S.R. spectroscopy, the presence of chromium (V) as an intermediate in the decomposition of praseodymium chromate (VI), facilities were not available for work at temperatures below 90°K. Because of the nature of the sample involved, this resulted in extremely broad spectral lines from which no definite conclusions could be drawn.

If the chromate (V) is formed as an intermediate in the decomposition of the chromate (VI) then in a partially decomposed sample of praseodymium chromate (VI), the following compounds would be present:-

(a) Undecomposed praseodymium chromate (VI)

(b) Praseodymium chromate (V)

(c) Praseodymium chromate (III)

(d) chromium (lll) oxide.

The e.s.r. spectrum from such a sample would be rather complex since all of the components, except the undecomposed chromate (VI) would show absorptions.

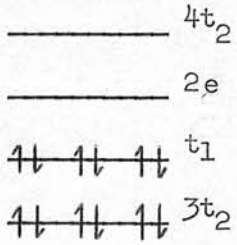
As a first step, the spectrum of each of the expected components was recorded, the samples being diluted by grinding with praseodymium chromate (VI), and at 90°K, the spectrum of each sample showed a single, very broad, absorption, all at approximately the same value of magnetic field. Spectra of samples of partially decomposed praseodymium chromate (VI) also showed, at 90°K, a single, very broad absorption, again in the same region of magnetic field. This indicates the presence in the partially decomposed chromate (VI) of one or more of the absorbing species mentioned above but it was not possible to deduce which of these were present. Had facilities for work at lower temperatures been available, it is possible that with the increased resolution obtained some meaningful information might have resulted from a study of intensities and line shapes, even if the absorptions of the individual components were not resolved. Such a study however was not considered worthwhile with the rather poor resolution available in this investigation.

DISCUSSION

The results obtained from the ultraviolet and visible and the infrared absorption spectra of the lanthanide chromates (V) and (III) and praseodymium chromate (VI) are discussed below.

The ultraviolet and visible spectra are of two types:- (a) those of the chromates (III) which have chromium (III) octahedrally co-ordinated by oxide ligands [Hahn and De Lorent (1957); Ruggiero and Ferro (1955)], where absorption bands are due to electronic transitions within the incomplete 3d level (d-d type spectra). (Chromates (V) in which chromium (V) d^1, is tetrahedrally co-ordinated by oxide ligands should also give d-d spectra.) (b) Those of the chromates (V) and praseodymium chromate (VI), where absorption bands are due to electronic transitions from the oxide ligands to the central metal atom [chromium (V) or (VI)] of the oxy-anion; such charge transfers give rise to much more intense absorption features than do d-d transitions.

The ultraviolet and visible spectrum of praseodymium chromate (VI) [Fig. VI] was interpreted on the basis of the molecular orbital energy level scheme for tetrahedral transition metal oxy-anions calculated by Viste and Gray (1964). The relevant portion of this energy level scheme is shown below:-



The first transition, $t_1 \longrightarrow 2e$, for the chromate (VI) ion in aqueous solution has been found to occur at 26,810 cm^{-1} [Carrington, Schonland and Symons (1957)] and is essentially the transfer of an

electron from a non-bonding oxygen π -orbital to an antibonding molecular orbital which is mainly metal in character i.e. this transition gives effectively reduction of chromium (VI) to chromium (V). The second transition, $3t_2 \longrightarrow 2e$, for the chromate (VI) ion in aqueous solution has been found to occur at 36,630 cm^{-1} [Carrington et al. (1957)].

This energy level scheme was calculated with respect to tetrahedral oxyanions, and although the exact structure of praseodymium chromate (VI) is unknown: it is possible that in the crystalline environment, the symmetry of the chromate (VI) groups is rather lower than tetrahedral. However, as shown in Fig. VI, only the two predicted absorptions, at approx. 27,500 and 36,000 cm^{-1} are present and therefore any further splitting of the energy levels due to site symmetry lower than T_d is too small to be resolved. Assignment of transitions therefore has been based on the assumption that the chromate (VI) ion retains full tetrahedral symmetry in this environment.

In a previous investigation [Darrie, Doyle and Kirkpatrick (1967)] the ultraviolet and visible spectra of the chromates (VI) of lanthanum, samarium and neodymium have been recorded and assignments made; and these results are shown in Table XI in comparison with the values found for praseodymium chromate (VI) in the present work.

TABLE XI

ASSIGNMENT OF FEATURES IN CHROMATE (VI) SPECTRA

Compound	Absorption Maxima			Assignment
	nm.	cm^{-1}	Intensity	
$La_2(CrO_4)_3.7H_2O$	370	27,000	v.s.	$t_1 \rightarrow 2e$
	275	36,300	s.	$3t_2 \rightarrow 2e$
$Pr_2(CrO_4)_3.hydr.$	365	27,400	v.s.	$t_1 \rightarrow 2e$
	270	37,000	v.s.	$3t_2 \rightarrow 2e$
$Nd_2(CrO_4)_3.7H_2O$	370	27,000	v.s.	$t_1 \rightarrow 2e$
$Sm_2(CrO_4)_3.hydr.$	370	27,000	v.s.	$t_1 \rightarrow 2e$
	280	35,700	s.	$3t_2 \rightarrow 2e$
$La_2(CrO_4)_3$	375	26,700	v.s.	$t_1 \rightarrow 2e$
	280	35,700	s.	$3t_2 \rightarrow 2e$
$Pr(CrO_4)_3$	355	28,200	v.s.	$t_1 \rightarrow 2e$
	280	35,700	v.s.	$3t_2 \rightarrow 2e$
$Nd_2(CrO_4)_3$	375	26,700	v.s.	$t_1 \rightarrow 2e$
$Sm_2(CrO_4)_3$	435	23,000	v.s.	$t_1 \rightarrow 2e$
	275	36,300	s.	$3t_2 \rightarrow 2e$

s = strong; v.s. = very strong.

Also present in the ultraviolet and visible spectra of hydrated and anhydrous praseodymium chromate (VI), as shown in Fig. VI, was a fairly weak, sharp absorption in the region 16,500 - 16,600 cm^{-1} which it is presumed from the line-shape is an f-f transition within the energy levels of the Pr^{3+} ion. The transition $^3H_4 \rightarrow {}^1D_2$ transition for the Pr^{3+} ion has been reported as occurring in the region of 16,580 - 16,640 cm^{-1} [Wong and Richman (1962)].

The ultraviolet and visible spectra of the lanthanide chromates (V) were also interpreted on the basis of the Viste and Gray (1964) energy level scheme, and the chromate (V) groups treated as having full T_d symmetry. The spectrum of the chromate (V) ion, CrO_4^{3-}, in alkaline solution was reported [Bailey and Symons (1957)] as showing two fairly broad absorption maxima, one at 16,000 cm^{-1} and the other at 28,200 cm^{-1}. The first of these was assigned by Viste and Gray (1964) as a $2e \rightarrow 4t_2$ transition, (since the chromium (V) d^1 configuration there is now an electron in the $3e$ level) which is essentially a d-d transition and the other assigned as $t_1 \rightarrow 2e$, a charge transfer which effectively reduces the chromium (V) to chromium (IV). The absorption maxima in the spectra of the lanthanide chromates (V) studied in the present work are shown in Tables XII and XIII, along with assignments and an estimate of intensities.

The only absorption which may be assigned with confidence is the $t_1 \rightarrow 2e$, charge transfer band occurring in the region of 25,000 cm^{-1} [Bailey and Symons (1957)]. It is possible that the band occurring in the region of 14,500 cm^{-1} may correspond to the $2e \rightarrow 4t_2$ transition, found to occur at 16,000 cm^{-1} in alkaline solution and the broad, rather weak absorption around 31,000 cm^{-1} may be assignable as the second charge transfer transition, $3t_2 \rightarrow 2e$. However, because of the rather poorly defined nature of these weaker bands it was considered inadvisable to make definite assignments for them.

TABLE XII

ASSIGNMENT OF FEATURES IN CHROMATE (V) SPECTRA

Compound	Absorption Maxima			Assignment
	nm.	cm^{-1}	Intensity	
$PrCrO_4$	815	12,300	w.	
	720	13,900	w.	
	395	25,300	s.	$t_1 \rightarrow 2e$
	330 sh.	30,000	w.	
$GdCrO_4$	840	11,900	w.	
	705	14,200	w.	
	400	25,000	s.	$t_1 \rightarrow 2e$
	325	30,800	w.	
	285	34,700	w.	
$TbCrO_4$	875	11,400	w.	
	720	13,900	w.	
	400	25,000	s.	$t_1 \rightarrow 2e$
	335 sh.	29,800	w.	
	295 sh.	33,900	w.	
$DyCrO_4$	850	11,800	w.	
	700	14,300	w.	
	405	24,700	s.	$t_1 \rightarrow 2e$
	320	31,250	w.	

w = weak s = strong sh = shoulder

TABLE XIII

(Continuation of Table XII)

ASSIGNMENT OF FEATURES IN CHROMATE (V) SPECTRA

Compound	Absorption Maxima			Assignment
	nm.	cm^{-1}	Intensity	
$HoCrO_4$	875	11,400	w.	
	700	14,300	w.	
	405	24,700	s.	$t_1 \rightarrow 2e$
	320	31,250	w.	
$ErCrO_4$	860	11,600	w.	
	695	14,400	w.	
	405	24,700	s.	$t_1 \rightarrow 2e$
	310	32,250	w.	
$YbCrO_4$	850	11,800	v.w.	
	675	14,800	w.	
	410	24,400	s.	$t_1 \rightarrow 2e$
	320	31,250	w.	
$YCrO_4$	850	11,800	w.	
	685	14,600	w.	
	400	25,000	s.	$t_1 \rightarrow 2e$
	320	31,250	w.	

w = weak v.w. = very weak s = strong

All of the chromates (III) studied in this work have chromium (III) octahedrally co-ordinated by oxide ligands, and the ultraviolet and visible spectra of these compounds were interpreted using an Orgel (1955) diagram for a d^3 ion in an octahedral field. The ground state for a field-free d^3 ion is a ^4F state which in a field of O_h symmetry splits into three quartet states, $^4A_{2g}(F)$, $^4T_{2g}(F)$ and $^4T_{1g}(F)$. There is only one other field-free quartet state, ^4P, which gives rise, in a field of octahedral symmetry, to only one state, $^4T_{1g}(P)$. The three strongest bands in the spectra of chromates (III) may be assigned to transitions from the $^4A_{2g}$ ground state to the other quartet states i.e. $^4A_{2g} \rightarrow {}^4T_{2g}(F)$; $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$. The energy of the first transition (i.e. of lowest energy), $^4A_{2g} \rightarrow {}^4T_{2g}$ has been shown to be equal to 10Dq [Tanabe and Sugano (1954)] i.e. the energy separation between the e_g and t_{2g} levels, since the configuration for the $^4A_{2g}$ state is $(t_{2g})^3$ and for the $^4T_{2g}$ state, $(t_{2g})^2 (e_g)^1$. Any weaker, low energy bands may be assigned to quartet doublet transitions occurring within the $(t_{2g})^3$ configuration. e.g. $^4A_{2g} \rightarrow {}^2E_g$; $^4A_{2g} \rightarrow {}^2T_{1g}$ and $^4A_{2g} \rightarrow {}^2T_{2g}$ in order of increasing energy.

These assignments are applicable to a d^3 ion in a field of octahedral symmetry, but in the chromates (III) studied here, it is likely that the chromium (III) ions will occupy sites of symmetry rather than O_h. If the site symmetry of the chromium (III) ions is lower than O_h, then considering the quartet states only, further splitting of the degenerate species might be expected. For example, the T_{2g} state in an O_h site, gives rise to A_{1g} and E_g states in D_{3d} symmetry, which will have slightly different energies [Wilson, Decius and Cross (1955)]. It can be seen from Fig. VII, that any splitting

which may occur due to lower symmetry is too small to be resolved and for convenience, assignments of these chromate (III) spectra are made as for a d^3 ion in octahedral symmetry. The value of Dq was found for each chromate (III) and using the Orgel diagram, the predicted energies of some of the assigned transitions were found. The measured values of absorption maxima (cm^{-1}), with an estimate of their relative intensities are shown in Table XIV. Also shown are the values for Dq and the predicted energies of the transitions.

No values were predicted for the quartet-doublet transitions, but the experimental values, in the range 13,500 - 14,600 cm^{-1} for values of Dq in the range 1613 - 1639 cm^{-1} agree quite well with results found for chromium (III) ions in various octahedral sites by Wood, Ferguson, Knox and Dillon (1963), viz. that the quartet-doublet transitions occurred at around 14,000 - 15,000 cm^{-1} for values of Dq in the range 1630 - 1800 cm^{-1}. Similarly it has been found, that for the complex ion $Cr(H_2O)_6^{3+}$ in aqueous solution, the $^4A_2 \rightarrow {}^2E$ transition occurs at 14,900 cm^{-1} and the $^4A_2 \rightarrow {}^2T_1$ transition at 15,100 cm^{-1} [Reinen and Schmitz - Du Mont (1961)].

TABLE XIV

ASSIGNMENT OF FEATURES IN THE CHROMATE (III) SPECTRAL

Compound	Assignment					
	$^4A_{2g} \downarrow {}^2E_g$ (cm^{-1})	$^4A_{2g} \downarrow {}^2T_{1g}$ (cm^{-1})	$^4A_{2g} \downarrow {}^4T_{2g}(F)$ (cm^{-1})	$^4A_{2g} \downarrow {}^4T_{1g}(F)$ (cm^{-1})	Charge Transfer and/or $^4A_{2g} \downarrow {}^4T_{1g}(P)$	
Pr CrO_3	13,700 w	14,300 w	16,130 s	21,280 s	27,400 s 29,410 s	Observed
Dq = 1613			16,130	24,200	37,800	Predicted
Gd CrO_3	13,510 w	14,500 w	16,130 s	21,740 s	27,400 s 31,250 s	Observed
Dq = 1613			16,130	24,200	37,800	Predicted
Tb CrO_3	13,660 w	14,600 w	16,260 s	21,980 s	27,400 s 30,770 s	Observed
Dq = 1626			16,260 s	24,500	38,000	Predicted
Dy CrO_3	13,510 w	14,500 w	16,260 s	21,740 s	27,780 s 31,250 s	Observed
Dq = 1626			16,260 s	24,500	38,000	Predicted
Ho CrO_3	13,510 w	14,500 w	16,260 s	21,740 s	27,780 s 31,250 s	Observed
Dq = 1626			16,260 s	24,500	38,000	Predicted
Er CrO_3	13,790 w	14,600 w	16,260 s	21,740 s	27,780 s 31,250 s	Observed
Dq = 1626			16,260 s	24,500	38,000	Predicted
Yb CrO_3	13,790 w	14,500 w	16,390 s	21,980 s	27,780 s 30,770 s	Observed
Dq = 1639			16,390	24,600	38,200	Predicted
Y CrO_3	13,510 w	14,500 w	16,260 s	21,740 s	27,780 s 31,250 s	Observed
Dq = 1626			16,260	24,500	38,000	Predicted

w = weak s = strong

The agreement between observed and predicted values of the energies for the $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ transition is reasonably good, but exact agreement is not expected since the construction of Orgel diagrams is based on Crystal Field Theory which considers metal-ligand bonding to be purely ionic whereas a certain degree of covalency is likely in these compounds. Some consideration was given to ascertaining the relative degrees of chromium (III) - oxide covalency in these compounds by use of the nephelauxetic ratio [Schaffer and Jorgensen (1958)], β, which is the ratio of the value of the Racah parameter B in a compound to its value in the free ion. The Racah parameters B and C, which are the electrostatic interaction parameters, may be measured from the spectrum as follows:-

(i) The energy difference from the ground state to the $^4T_{2g}$ state represents 10 Dq

(ii) The energy of the transition $^4A_{2g}$ (ground state) $\longrightarrow {}^4T_{1g}(F)$ is approximately equal to 10 Dq + 12 B [Tanabe and Sugano (1954)].

(iii) The value of C is approximately fixed by the location of the ^2E_g level which occurs at an energy equal to 9B + 3C above the ground state.

There is a third Racah parameter, A, which enters into the formulation of all terms of the d^3 configuration in the same way and so can be factored out. The 'free' Cr^{3+} ion value of B, designated B^1, has been found equal to 920 cm^{-1} and the free ion value of C, designated C^1, equal to 3,680 cm^{-1} (i.e. free ion ratio of $\frac{C}{B} = 4.0$) [Wood et al. (1963)]. The values of B, C, the ratio $\frac{C}{B}$ and the nephelauxetic ratio, $\beta = \frac{B}{B^1}$ for the chromates (III) studies, are shown in Table XV.

TABLE XV

RACAH PARAMETERS FOR CHROMATES (III)

Compound	B (cm^{-1})	C (cm^{-1})	$\frac{C}{B}$	$\beta = \frac{B}{B_1}$
$PrCrO_3$	429	3280	7.65	0.47
$GdCrO_3$	468	3099	6.62	0.51
$TbCrO_3$	477	3122	6.55	0.52
$DyCrO_3$	457	3132	6.85	0.50
$HoCrO_3$	457	3132	6.85	0.50
$ErCrO_3$	457	3226	7.06	0.50
$YbCrO_3$	466	3199	6.86	0.51
$YCrO_3$	457	3132	6.85	0.50

In their studies of the spectrum of chromium (III) in different octahedral environments, Wood et al. (1963) found values of the Racah parameter B which varied from 370 - 780 cm^{-1} as compared with the free ion value of 920 cm^{-1}. They concluded that this decrease in electrostatic interaction in the crystal was presumably due to orbital expansion caused by the presence of the ligand atoms. This decrease has been related [Schaffer and Jorgensen (1958)] to covalency, which also involves orbital expansion. It can be seen from Table XV that there is a certain variation in the values of the ratio $\frac{C}{B}$.

"The alteration of the e and t_2 molecular orbitals due to differential expansion of the metallic basis kd orbitals and to selective modification of the covalent linkage of the addend orbitals because of structural and steric effects and incompatibilities (such as fixture of a transition metal ion in too large or too small a lattice

hole or a distorted site) induces strong fluctuations in the electron-electron repulsive forces as measured by the Racah parameters B and C, and hence the vacillation of the ratio C/B ". It was concluded by Wood et al. (1963) that if the orbital expansion becomes considerable, then the requirement in the theory that the e_g and t_{2g} orbitals must have the same radial distribution for the electron repulsion parameters to be reduced to only two (B and C), becomes invalid. It is therefore dangerous to attempt quantitative calculations relating the nephelauxetic ratio to covalency. However since in the compounds studied here, the ligand (oxide) always remains the same, it seems reasonable to, at least qualitatively, use these ratios to determine the relative degrees of covalency of the chromium (III) - oxygen band. From Table XV, this order is seen to be:-

$PrCrO_3 > DyCrO_3 \simeq HoCrO_3 \simeq ErCrO_3 \simeq YCrO_3 > GdCrO_3 \simeq YbCrO_3 > TbCrO_3$

The degree of covalency of these compounds is likely to be effected by the polarising power of the accompanying cation i.e. the greater the polarising power of cation, the greater its attraction for the oxide ions, and hence, the lower the covalency of the chromium-oxide band. The polarising power of the cation may be measured by e/r^2 and for the lanthanide ions studied, the values are as shown in Table XVI [Ferraro and Walker (1965)].

TABLE XVI

POLARISING POWER OF THE CATIONS IN THE CHROMATES (III)

Compound	Cation	Ionic Radius (Å)	e/r^2
$PrCrO_3$	Pr^{3+}	1.01	2.94
$GdCrO_3$	Gd^{3+}	0.94	3.40
$TbCrO_3$	Tb^{3+}	0.92	3.54
$DyCrO_3$	Dy^{3+}	0.91	3.62
$HoCrO_3$	Ho^{3+}	0.89	3.79
$YCrO_3$	Y^{3+}	0.90	3.70
$ErCrO_3$	Er^{3+}	0.88	3.87
$YbCrO_3$	Yb^{3+}	0.86	4.07

These values of polarising power of the cations would place the order of covalency of the chromates (III) as follows:-

$PrCrO_3 > GdCrO_3 > TbCrO_3 > DyCrO_3 > YCrO_3 > HoCrO_3 > ErCrO_3 > YbCrO_3$

On comparison with the order found using the nephelauxetic ratios, it is seen that the values for the chromates (III) of gadolinium and terbium are rather out of order, but praseodymium chromate (III) comes first in each case, and the chromates (III) of dysprosium, yttrium, holmium and erbium retain approximately the correct order. It is not however, surprising that some deviations occur considering the rather small differences in properties of the rare earth cations.

The infrared absorption spectra of the hydrated and anhydrous chromates (VI) of lanthanum, samarium and neodymium have been described by Darrie et al. (1967) and the absorption maxima for these are shown with the values found for praseodymium chromate (VI) in the present work [Table VII]. The fundamental frequencies of the chromate (VI)

ion in aqueous solution have been found [Stammreich, Bassi and Sala (1958)] to be as follows:-

$\nu_1(a_1)$	$\nu_2(e)$	$\nu_3(f_2)$	$\nu_4(f_2)$	
847	348	884	368	cm^{-1}

so that in the range studied in the present work, 2000-400 cm^{-1}, only ν_1, the symmetric stretching vibration, and ν_3, the asymmetric stretching vibration would be expected. In T_d symmetry, only ν_3 the asymmetric stretch would be infrared active, but in hydrated and anhydrous praseodymium chromate (VI), the site symmetry of the chromate (VI) groups, although unknown, is likely to be lower than T_d and it might reasonably be expected that ν_1 would become infrared active. The ν_3 asymmetric stretching vibration is triply degenerate in T_d but again if the site symmetry of the chromate (VI) ion is lower than T_d, splitting of the degeneracy may occur.

For hydrated praseodymium chromate (VI), the strong band at 920 cm^{-1} has been assigned to ν_3 and the medium band at 865 cm^{-1} to ν_1 [Darrie et al. (1967)]. The medium band at 1630 cm^{-1} is assigned to the bending mode of the lattice water, which is known to occur in the range 16300 - 16000 cm^{-1} [Nakamoto (1963)]. The bands at 850 and 825 cm^{-1} are probably the rocking modes of water co-ordinated to the cation [Nakagawa and Shimanouchi (1964)] and the band at 625 cm^{-1} the lattice water wagging mode, which like the rocking mode, varies with the cation to which the water is co-ordinated [Nakagawa and Shimanouchi (1964)]. A summary of these assignments is shown for praseodymium chromate (VI) in Table XVII.

TABLE XVII

ASSIGNMENT OF SPECTRAL FEATURES OF HYDRATED AND ANHYDROUS PRASEODYMIUM CHROMATE (VI)

$Pr_2(CrO_4)_3$.Hydr.	$Pr_2CrO_4)_3$	Assignment
1630 m.br.		H_2O bend
	1005 m.	
920 s.	940 s.	$\nu_3(f_2)$
865 m.	860 m.	$\nu_1(a_1)$
850 m.		)
		) OH_2 rock
825 m.		)
	790 s.br.	
625 w.br.		OH_2 wag
	455 m.	
	435 m.	

For anhydrous praseodymium chromate (VI), the strong band at 940 cm^{-1} has been assigned to ν_3 and the medium band at 860 cm^{-1} to ν_1, as shown in Table XVII. This leaves to be explained, the medium band at 1005 cm^{-1}, the strong band at 790 cm^{-1} and the two medium bands at 455 and 435 cm^{-1}. The infrared spectra of a number of chromates (VI) have been studied by Campbell (1965). Some of these chromates (VI) have the $CrVO_4$ structure [Brandt (1943)], so that the chromium is in a C_{2v} site and these chromates (VI) all have bands in the region 760 - 820 cm^{-1} which cannot be assigned to either ν_1 or ν_3 of the chromate ion. Campbell (1965) observed that these spectra are similar in appearance to those of dichromates because of the bands in the region 760 - 820 cm^{-1} and assigned these 'extra' bands for the chromates (VI)

as being due to strong M^{II} - O covalency and hence representing M^{II} - O - Cr^{VI} stretching c.f. the Cr^{VI} asymmetric stretch of the dichromate ion which occurs at 795 cm^{-1} for the aqueous ion [Stammreich, Bassi, Sala and Siebert (1958)]. Darrie et al. (1967) have however assigned these 'extra' bands in the spectra of chromates (VI) of magnesium, lanthanum, samarium and neodymium as being due to the effects of anion-anion coupling. Magnesium chromate (VI) has the $CrVO_4$ structure [Brandt (1943)] in which there are chains at MO_6 octahedra linked by rows of chromate tetrahedra giving a likelihood of anion-anion coupling and by analogy with this Darrie et al. (1967) made a similar assignment for the lanthanide chromates (VI). There is no obvious explanation for the medium band at 1005 cm^{-1} in the spectrum of anhydrous praseodymium chromate (VI), although a similar band has been found for anhydrous magnesium chromate (VI). The bands in the region 450 - 250 cm^{-1} of a number of chromates (VI) have been assigned [Campbell (1965)] to the bending vibrations of chromate (VI) and this seems the most likely explanation for the bands found at 455 and 435 cm^{-1} in the present work.

The infrared spectra of some lanthanide chromates (V) are now discussed in terms of the symmetry [Halford (1946)] of the chromate ion in the lattice. The only assignment which has been made for the chromate (V) ion in aqueous solution [Guerchais, Leroy and Rhomer (1965)] is the ν_3 (f_2) asymmetric stretch, at 675 cm^{-1}, which is triply degenerate in T_d but whose degeneracy may be removed by the lowered symmetry of the chromate (V) ion in the lattice. The positions of the absorption maxima (cm^{-1}), with an estimate of their intensities, and the assignments made for these lanthanide chromates (V) is given in Table XVIII, using the results of the KBr disk spectra only. These lanthanide chromates (V) all have the tetragonal

zircon structure [Schwarz (1963) ; Buisson et al. (1964)] with the exception of praseodymium chromate (V) which shows X-ray diffraction lines corresponding to the zircon structure and also to the monoclinic Huttonite structure [Schwarz (1963)]. Those chromate (V) groups in praseodymium chromate (V) with Huttonite structure (space group $P2_1/n$ - c_{2h}^5) are isostructural with lanthanum phosphate [Mooney (1948)] in which the phosphate ions are on sites of C_1 symmetry [Hezel and Ross (1966)] which will therefore also be the symmetry of some of the chromate (V) groups in praseodymium chromate (V). In C, symmetry, ν_1, ν_2, ν_3 and ν_4 are all infrared active although ν_2 and ν_4 will probably occur below 400 cm^{-1}.

TABLE XVIII

ASSIGNMENT OF SPECTRAL FEATURES FOR LANTHANIDE CHROMATES (V)

$PrCrO_4$	$GdCrO_4$	$TbCrO_4$	$DyCrO_4$	$HoCrO_4$	$ErCrO_4$	$YbCrO_4$	$YCrO_4$	Assignment
	943 w.		950 w.					
	861 w.sh.	866 w.sh.	860 w.sh.					
838 w.sh.	838 w.sh.	838 w.sh.		835 w.sh.	836 w.sh.	859 w.sh.	850 w.sh.	)
								)
								) ν_3
788 m.br.	770 s.	779 s.	777 s.	780 s.	780 s.	783 s.	780 s.	)
732 s.								ν_1

w = weak; s = strong; m = medium; sh = shoulder

The other lanthanide chromates (V) studied, and in part praseodymium chromate (V), have the tetragonal zircon structure (space group $I4_1/amd$ - D_{4h}^{19}) with the chromate ions on sites of D_{2d} symmetry. The correlation table for T_d and D_{2d} [Wilson, Decius and Cross (1955)] is given below.

	T_d	D_{2d}
ν_1	A_1	A_1
ν_2	E	$A_1 + B_1$
ν_3	F_2	$B_2 + E$
ν_4	F_2	$B_2 + E$

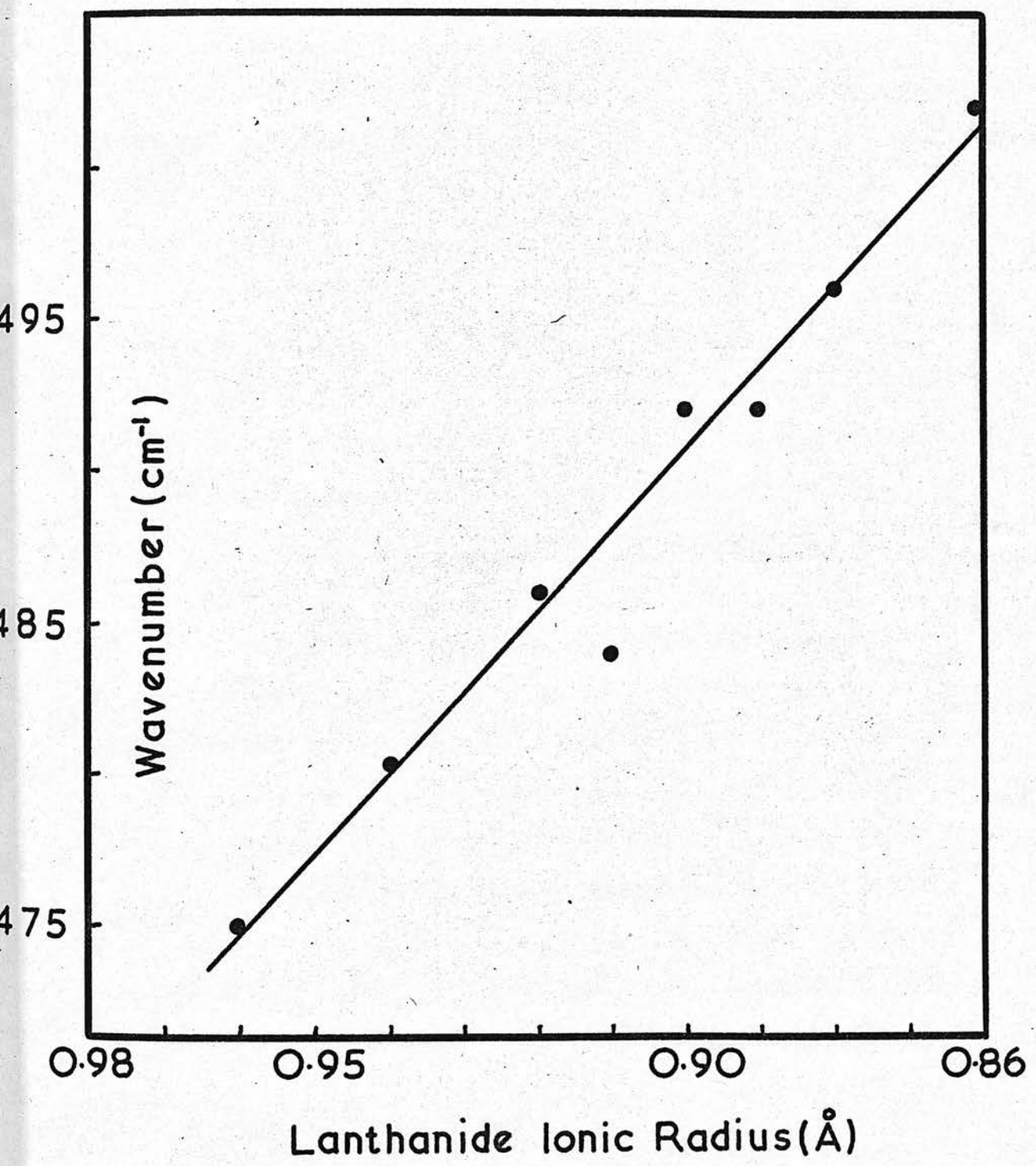
In D_{2d}, only the B_2 and E vibrations are infrared active [Herzberg (1956)] and this explains why only for praseodymium chromate (V) is the ν_1 vibration visible, being allowed for those chromate (V) groups which have C_1 site symmetry. For the other chromates (V), the weak feature occurring in the range 835 - 860 cm^{-1} is probably the B_2 band, expected to be weaker and sharper than the double degenerate E band, which will be contained in the broad strong feature in the range 770 - 788 cm^{-1}. Still to be accounted for are the weak bands at 943 and 861 cm^{-1} for gadolinium chromate (V), at 866 cm^{-1} for terbium chromate (V) and at 950 and 860 cm^{-1} for dysprosium chromate (V). It is difficult to account for the presence of those weak bands at 943 cm^{-1} for gadolinium chromate (V) and at 950 cm^{-1} for dysprosium chromate (V). The presence of the weak bands at around 860 cm^{-1} might however be explained in terms of combination bands of the species of the ν_2 and ν_4 vibrations several of which are infrared active in D_{2d} symmetry [Hezel and Ross (1966)]. The positions of the ν_2 and ν_4 vibrations are unknown, but will probably occur in the region 300 -

400 cm^{-1}. It has been suggested that the width of the E species of the ν_3 transition in the chromates (V) of samarium and neodymium [Darrie (1967)] may be due to anion-anion coupling, but the distance between neighbouring chromate (V) groups in the zircon structure may well be too large to permit direct anion-anion interaction.

There is at present no comprehensive theory available with regard to the vibrational spectra of the lanthanide chromates (III). A previous investigation [Matveichuk, Shevchenko and Skripchenko (1966)] on the infrared spectra of the complete series of lanthanide chromates (III) showed that the spectra of all these compounds showed two intense bands in the region 700 - 400 cm^{-1}. The band at 600 cm^{-1} was assigned as the stretching vibration of the Cr - O band, and was the same in all compounds. The second band at 480 - 430 cm^{-1} was found to be a singlet in chromates (III) of the cerium subgroup and split into a doublet, triplet or quartet in the yttrium subgroup. The splitting was considered to be due to perturbation by the lattice and the band assigned to a lanthanide - oxide - chromium stretching vibration, since the frequency of this second band was found to be linearly related to the ionic radii of the lanthanide ions. The results from the present work [Table VI] indicate that the first band is actually at least a doublet, with the maximum of one species in the range 610 - 620 cm^{-1} and of another species in the range 580 - 590 cm^{-1}. The second band appears to be a doublet or triplet and a plot of lanthanide ionic radius against the frequency of the species which occurs in the range 480 - 502 does indicate a linear relationship [Fig. XIII] and the assignment as Ln^{3+} - O - Cr^{3+} stretch seems reasonable.

FIG. XIII

IONIC RADIUS vs. WAVENUMBER OF 2nd. I.R. ABSORPTION BAND FOR SOME LANTHANIDE CHROMATES(III)



SECTION II

THERMAL DECOMPOSITION OF SOME CHROMATES (V) AND PRASEODYMIUM CHROMATE (VI)

INTRODUCTION

THERMAL DECOMPOSITION OF SOME LANTHANIDE CHROMATES (V) AND PRASEODYMIUM CHROMATE (VI)

Many oxy-salts, on heating, decompose according to the equation:-

$$A\ (solid) \longrightarrow B\ (solid) + C\ (gas)$$

Two methods are available for following the course of such decompositions:-

(a) continuous measurement of weight loss of the sample due to evolution of C (gas)

(b) continuous measurement of pressure developed by C (gas) as the reaction proceeds

Method (a) may be used under vacuum or at normal pressures in an atmosphere of any suitable gas, whereas method (b) may be used under vacuum conditions only.

Kinetic studies of chemical processes which occur in the homogeneous phase have shown that reaction rate is often directly proportional to the reactant molecules concentration raised to a power. Most heterogeneous reactions, including the reactions of solids, do not, in general, obey these kinetic laws in which rate is dependent on the power of reactant concentration. More usually, reactions involving solids occur at a reactant-product interface and this results in characteristic kinetic properties. These rates usually depend on (a) Rate of nucleation and (b) Rate of growth of nuclei; reaction kinetics may also be influenced by the average crystallite size and the particle size distribution about this value. [Galwey (1967)].

In reactions of the type:- $A\ (solid) \longrightarrow B\ (solid) + C\ (gas)$ the onset of the reaction involves the formation of the new phase, B, at special points in the lattice of A. Decomposition will commence when local fluctuations provide favourable circumstances for the formation of B. The first formed fragments of B embedded in a matrix

of A may retain the molecular volume and lattice type of A while larger particles of B will generally possess a different molecular volume and lattice type to that of A causing strain by local deformations of the lattice. As a consequence of this strain, small fragments of B may become unstable and tend to revert back to A whereas large fragments of B will be stable. As a result of this, further reaction tends to take place at the boundary between the two solid phases rather than lead to the initiation of a large number of small fragments of B. The product phase thus spreads outwards from these points where reaction first commences and these points are referred to as 'nuclei'. As reaction progresses, the area of the reactant-product interface is reduced due to overlap of product nuclei, bringing about a decrease in the reaction rate. In some cases, clustering of nuclei occurs [Harvey. (1933)] and may mean that such centres are formed from each other; in others, the appearance of rows of nuclei [Wischin (1939)] suggests that there are favoured places, such as along surface cracks or lines of strain, where formation is preferred.

The first stage in the study of the kinetics of a solid state decomposition is the construction of a plot of fraction of sample decomposed (x) against time (t). Such a curve (the 'x - t' curve) may have one of a number of shapes [Jacobs and Tompkins (1955)], depending on the nature of the decomposition, and the shape of the curve gives an indication of which of the possible rate laws might apply to a particular decomposition. Rate laws derived from consideration of the formation and growth of product nuclei have previously been reviewed by Jacobs and Tompkins (1955). The rate law chosen for a particular decomposition is that which best fits the experimental data although normally a fit over only a limited range of decomposition is found [Hume and Colvin (1931)], and in many cases different rate

laws may be found to fit for different parts of the decomposition curve [Yankewich and Zavitsanos (1964)].

The most common method for studying the kinetics of a solid state decomposition is to decompose samples of the compound isothermally at a series of temperatures and find, from rate law application, the value for k - the rate constant - at each temperature. Hence, using the Arrhenius equation:- $k = Ae^{-E/RT}$, a value for the energy of activation for the decomposition may be obtained. A non-isothermal method for studying solid state decompositions [Coats and Redfern (1964)] requires much less data than the isothermal method, involving the decomposition of only a single sample, but the sample temperature rise must be linear with time and thus very small samples must be used to minimise the effect of any endo- or exo-thermic changes in the sample.

No general quantitative formula for the influence of particle size on reaction kinetics has yet been established but some general conclusions have been drawn [Galwey (1967)] from the information available.

(a) Nucleation is favoured by an increase in reactant surface area, so that, at first, reaction rate is increased by a reduction in particle size.

(b) After a certain crystallite size has been reached, further reduction limits the volume of material decomposed following nucleation on a particular crystallite.

The alkali metal chromates (VI) are all extremely stable to heat. Sodium chromate (VI) melts at 800°C [Nayar, Watson and Sudborough (1924)] and shows no signs of decomposition even after prolonged heating at 1000°C, while potassium chromate (VI) melts without decomposition at 984°C [Schemtschuschny (1908)]; of the other univalent metal chromates (VI), that of thallium is stable to at

least 745°C (m.p. = 633°C) [Duval and Peltier (1948)]; mercury (I) chromate (VI) is stable up to 256°C, but between 256 and 671°C loses oxygen and mercury leaving a residue of chromium (III) oxide [Dupuis and Duval (1949)].

Some divalent metal chromates (VI) are also quite stable to heat: lead (II) and barium chromates (VI) are stable to over 900°C [Dupuis and Duval (1949)] and calcium chromate (VI) shows no signs of decomposition when heated at 1,000°C [Nayar et al. (1924)]. Charcosset, Turlier and Trambouze (1964) reported that nickel chromate (VI) is stable to about 1,000°C in air and they studied thermo gravimetrically the decomposition in air of copper (II) chromate (VI) over the range 403 - 449°C.

It has previously been reported [Schwarz (1963)] that the lanthanide chromates (VI) decompose in two stages according to the general equations:-

$$Ln_2(CrO_4)_3 \longrightarrow 2\ LnCrO_4 + 0.5\ Cr_2O_3 + 1.25\ O_2 \quad \ldots\ldots \text{(I)}$$

$$2\ LnCrO_4 \longrightarrow 2\ LnCrO_3 + O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(II)}$$

with the exception of praseodymium chromate (VI) where thermal analysis indicated no thermally stable chromate (V) intermediate. A more detailed study of the kinetics of the thermal decomposition of some lanthanide chromates (VI) has been reported by Darrie, Doyle and Kirkpatrick (1966), in which details of the kinetics of isothermal decompositions of the chromates (VI) of lanthanum, samarium and neodymium have been given. For lanthanum and samarium chromates (VI) both stages of decomposition were examined, while for neodymium chromate (VI), the first stage only was reported. The first stage of decomposition of lanthanum chromate (VI) was studied isothermally in the temperature range 580 - 630°C; of neodymium chromate (VI) in the range 570-627°C;

and of samarium chromate (VI) in the range 520 - 572°C. The second stage of decomposition of lanthanum chromate (VI) was studied isothermally in the range 630 - 700°C; and of samarium chromate (VI) in the range 670 - 720°C. Thermal activation energies for first and second stages of decomposition were compared, and found to be in good agreement, with the energies of charge-transfer bands in the ultraviolet spectra. This was interpreted as indicating that the activation process in these decompositions involved electron-transfer from oxygen to chromium. The differences in thermal stability of these lanthanide chromates (VI) from other more thermally stable chromates (VI) were explained as being of a structural nature. Only in chromates (VI) having the $CrVO_4$ structure with rows of chromate (VI) tetrahedra [Brandt (1943)] will the activation process be readily transmitted to the surface, where decomposition commences.

A similar study has been reported for the chromates (V) of lanthanum, neodymium and samarium [Darrie (1967)]. Agreement between thermal activation energy and charge-transfer energy was found for lanthanum chromate (V) only and it was postulated that some process other than electron-transfer must be involved in the activation step for the decomposition of the chromates (V) of neodymium and samarium. Schwarz (1963) has reported that the limits of thermal stability of the lanthanide chromates (V) and yttrium chromate (V) lie within a fairly narrow temperature range - from 640°C for lanthanum chromate (V) to 690°C for dysprosium chromate (V), but no detailed investigation of the decomposition of rare earth chromates (V), other than those of lanthanum, neodymium and samarium, has previously been reported.

Of the salts of other transition metal oxyanions, only the thermal decomposition of permanganates has been studied in detail. Thermal decomposition, under vacuum, of whole and ground crystals of potassium

permanganate was studied by Prout and Tompkins (1944) who found that the results best fitted the equation:- $\log \frac{x}{1-x} = kt + c$ (x = fraction decomposed; t = time; k and c were constants). Thermal decomposition of rubidium [Herley and Prout (1960)] and caesium [Herley and Prout (1959)] permanganates were also found to fit this equation, while results for the decomposition of silver permanganate were best fitted [Prout and Tompkins (1946)] by the modified equation:-

$$\log \frac{x}{1-x} = k \log t + c$$

The mechanism proposed for the decompositions of the permanganates of potassium, caesium, rubidium and silver was based on the mobility of electrons which were considered to transfer from an oxygen of the permanganate ion to the accompanying cation [Prout and Tompkins (1944)]. Grinding of samples [Prout and Tompkins (1944)] and γ-irradiation prior to heating [Prout and Sole (1959); Prout (1958)] led to a shortening of the induction period and an increase in the rate of decomposition at any temperature. Pre-irradiation was considered [Prout (1958)] to aid decomposition by creation of lattice defects brought about by displacement of cations.

An alternative mechanism [Boldyrev et al. (1966)] for the decomposition of potassium permanganate postulated an electron-transfer between anions, according to the equation:-

$$2\ MnO_4^- \longrightarrow MnO_4^{2-} + MnO_4^{\circ}$$

The manganate (VI) ion is more stable than permanganate but MnO_4° decomposes to manganese dioxide and oxygen. Addition of manganate (VI) ion inhibits the decomposition but manganese dioxide accelerates it, probably by acting as an electron acceptor in the permanganate lattice. The increased rate of decomposition on pre-irradiation is considered [Boldyrev and Oblivantsev (1962)] to be due to small amounts of decomposition products formed on radiolysis rather than due

to displacement of cations in the lattice since pre-irradiation with energies less than required for cation displacement cause an increase in rate of thermal decomposition.

Experimental Methods

The isothermal decompositions of praseodymium chromate (VI) and the lanthanide chromates (V) were examined over a range of temperatures, using a Stanton-Mossflow M.F.H. - 1 automatic recording thermobalance. The samples were placed in the instrument in a platinum crucible, using approximately the same weight of sample in each case (ca. 1.000 gms). It had previously been shown [Darrie (1967)] that sample size has no effect on the rate of decomposition, but 1.000 gms. was regarded as being the minimum weight compatible with minimising the effects of instrument error. In the series of lanthanide chromates (V) studied in the present work, each compound was subjected, during preparation, to approximately the same amount of grinding in an attempt to ensure that particle size was fairly consistent throughout the series of compounds. Each sample was placed in the furnace and heated up to the selected temperature as it had previously been found [Darrie (1967)] that with the instrument used, a temperature overshoot occurs if the furnace is heated and the sample then introduced at the working temperature. Using the technique of heating the sample from room temperature, on switching the instrument to isothermal conditions, a temperature overshoot of approximately $+5^{\circ}C$ was observed but temperatures settled fairly quickly and thereafter were accurate to $\pm 1^{\circ}C$. Weight loss readings were taken to be accurate to $\pm$ 0.5 mgms. All isothermal runs were allowed to proceed for 240 mins, with continuous weight recording and the data from these used for the construction of 'x - t' curves.

Since experimental weight losses for the lanthanide chromates (V) agreed, within experimental error, with calculated values, the values taken as representing 100% weight loss for these compounds were those calculated according to the equation:-

$$LnCrO_4 \rightarrow LnCrO_3 + 0.5O_2$$

In the thermal decomposition of praseodymium chromate (VI), no indication was obtained, from isothermal runs, of a flattening off of the 'x - t' curve, which could be taken as showing completion of a first stage of decomposition. For the purposes of kinetic studies, therefore, it was decided to use, as a value for 100% decomposition, the weight loss calculated from the equation:-

$$Ln_2(CrO_4)_3 \rightarrow 2\ LnCrO_4 + 0.5\ Cr_2O_3 + 1.25O_2$$

- thereby assuming that the initial part of the decomposition of the praseodymium chromate (VI) results in the formation of praseodymium chromate (V) with no simultaneous decomposition to praseodymium chromate (III). It will be shown later, from X-ray diffraction work on partially decomposed samples of praseodymium chromate (VI), that this assumption is to some extent justified.

The effect of ageing on the rate of decomposition of a sample was observed for praseodymium chromate (VI). Isothermal runs at the same temperatures on samples from the same batch of material showed that after one year, the compound decomposed more slowly than when it was freshly prepared. The values of rate constants obtained from a power law applied to the decomposition of the compound demonstrate this effect Table XIX .

TABLE XIX

RATE CONSTANTS FOR THE DECOMPOSITION OF $Pr_2(CrO_4)_3$

Temperature (°C)	Rate Constant (k) min^{-1}	
	Freshly Prepared	After one year
580	0.0040	
594	0.0095	
600	0.0151	0.0050
610	0.0182	0.0111
617		0.0153

The isothermal decompositions of the lanthanide chromates (V) and praseodymium chromate (VI) were examined at the following temperatures:-

Praseodymium chromate (VI):-	594, 599, 600, 603, 606, 615, 617, 618, 627 °C.
Praseodymium chromate (V):-	616, 622, 626, 628, 630, 637, 640, 641, 647, 650 °C.
Gadolinium chromate (V):-	700, 706, 711, 716, 720, 723, 727, 736 °C.
Terbium chromate (V):-	641, 647, 650, 656, 658, 664, 667, 673, 682 °C.
Dysprosium chromate (V):-	635, 638, 641, 644, 646, 648, 650, 655, 660, 672 °C.
Holmium chromate (V):-	649, 655, 660, 662, 665, 668, 670, 675, 680, 686 °C.
Erbium chromate (V):-	652, 659, 661, 667, 670, 675, 677, 680, 690 °C.
Ytterbium chromate (V):-	634, 637, 641, 647, 650, 652, 654, 661, 670 °C.
Yttrium chromate (V):-	651, 656, 658, 660, 662, 665, 670, 680, 701 °C.

For each compound, some of the partially decomposed samples from the isothermal decompositions were examined by X-ray diffraction, Infrared spectroscopy and magnetic susceptibility measurements in an attempt to identify any reaction intermediates. This was of particular importance in the decomposition of praseodymium chromate (VI) where it was hoped to find some evidence for the presence of the chromate (V) intermediate.

RESULTS FROM ISOTHERMAL DECOMPOSITIONS

The results are given below for the isothermal decompositions of the lanthanide chromates (V) and praseodymium chromate (VI), the preparations of which were discussed earlier. For each compound, various rate laws were applied to the fraction decomposed (x) - time (t) data. The rate laws applied were as follows:-

(a) The power law [Jacobs and Tompkins (1955)] in the form $x = (kt)^n$ where n is a constant and k is the rate constant.

(b) The Prout-Tompkins equation [Prout and Tompkins (1944)] in the form $\log \frac{x}{1-x} = kt + c$ where c is a constant and k is the rate constant.

(c) The contracting plate equation [Jacobs and Tompkins (1955)] in the form $1 - (1-x)^{\frac{1}{2}} = \frac{k}{a} t$ where k is the rate constant and 'a' is the length of the side of a reactant particle in the shape of a square plate or the radius of a circular plate-shaped particle.

(d) The contracting sphere equation [Jacobs and Tompkins (1955)] in the form $1-(1-x)^{\frac{1}{3}} = \frac{k}{a} .t$ where k is the rate constant and 'a' is the radius of spherical reactant particles.

(e) The first order rate law in the form $\log_{10} \frac{1}{1-x} = kt$ where k is the rate constant.

For each chromate studied, the rate constant at each temperature was calculated from those rate laws which best fitted the 'x-t' data. By application of the Arrhenius equation, in the form $k = s\, e^{-E/RT}$ [Jacobs and Tompkins (1955)], where k is the rate constant, s is the entropy factor $= e^{\Delta S/R}$; E is the thermal activation energy and T is the absolute temperature, the activation energy, E, for the decom-

position was calculated by plotting the logarithm (base 10) of the rate constant against the reciprocal of the absolute temperature. The best straight line through the experimental points was calculated by the method of least squares and is of slope $-\frac{E}{2.303R}$

The errors quoted for activation energies and rate constants were determined by calculating the errors in values due to the error in weight readings of $\pm$ 0.5 mgms. The errors in rate constants were then calculated from maximum and minimum values of x, and the errors in activation energies obtained by combining the errors in rate constants with the error in temperature readings of $\pm$ 1°C.

ISOTHERMAL DECOMPOSITION OF PRASEODYMIUM CHROMATE (VI)

The isothermal decomposition of anhydrous praseodymium chromate (VI) was studied in the temperature range 594 - 628°C, and 'x-t' curves were plotted for the complete decomposition [Fig. XIV] according to the equation:-

$$Pr_2(CrO_4)_3 \longrightarrow 2\ PrCrO_3 + 0.5\ Cr_2O_3 + 2.25O_2$$ [Schwarz (1963)]

These curves showed no indication, e.g. levelling in the middle of the curve, of a region corresponding to formation of stable praseodymium chromate (V). A further set of 'x-t' curves was then constructed using as the value for 100% decomposition, the weight loss calculated according to the equation:-

$$Pr_2(CrO_4)_3 \longrightarrow 2\ PrCrO_4 + 0.5\ Cr_2O_3 + 1.25\ O_2$$

These curves, shown in Fig. XV, show an initial acceleratory period, followed by a deceleratory stage. On application of the various rate laws, the best fit for the experimental data was found using a power law of the type $x=(kt)^n$. From plots of Log_{10} x against log_{10} t [shown in Fig. XVI] values of n were calculated and are shown in Table XX below.

FIG. XIV

FRACTION DECOMPOSED(x)-TIME(t) CURVES FOR THE DECOMPOSITION OF $Pr_2(CrO_4)_3$

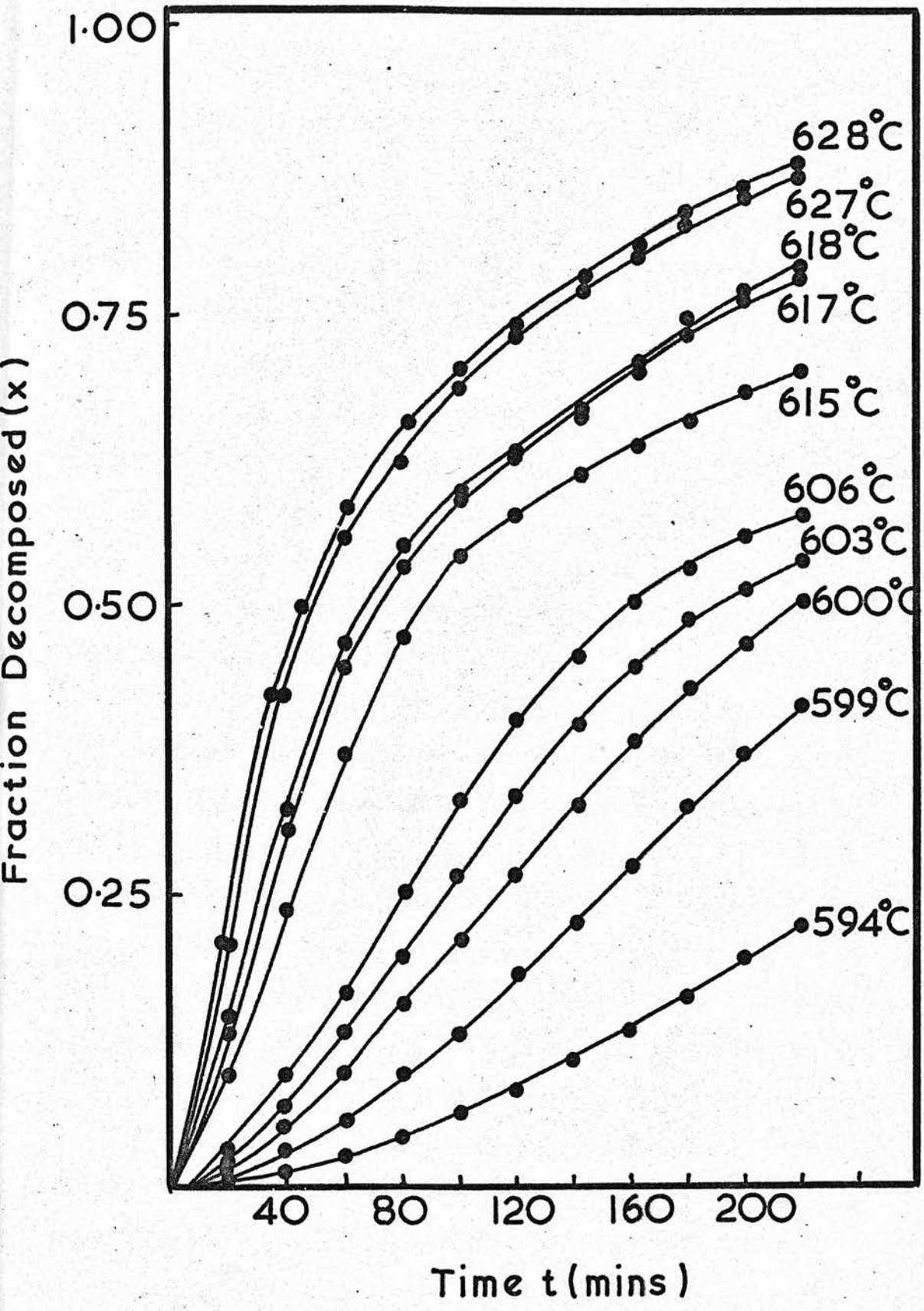


FIG. XV

FRACTION DECOMPOSED(x)-TIME(t) CURVES FOR THE DECOMPOSITION OF $Pr_2(CrO_4)_3$-FIRST STAGE.

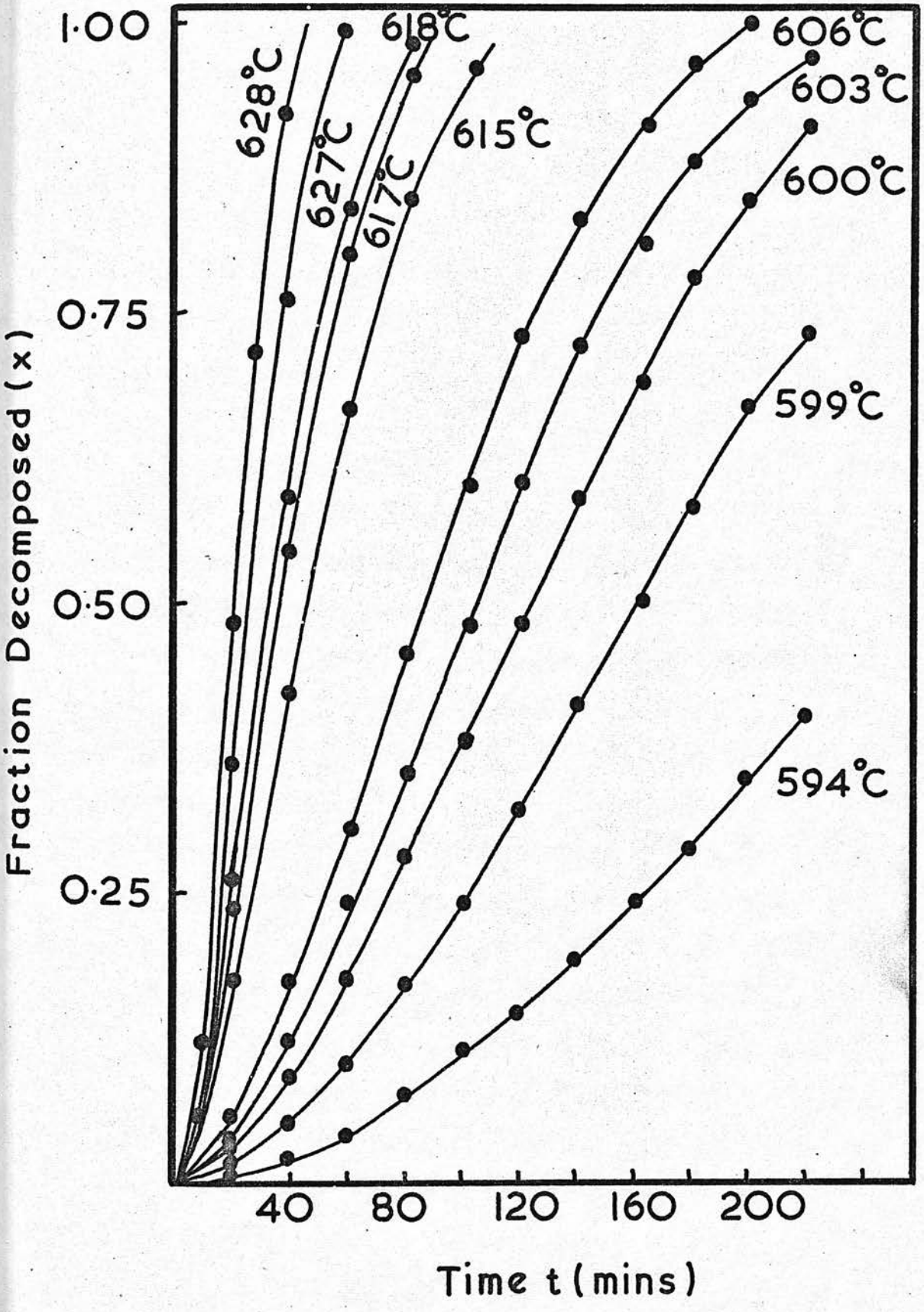


TABLE XX

VALUES OF n FOR THE POWER LAW APPLIED TO THE FIRST STAGE OF DECOMPOSITION OF $Pr_2(CrO_4)_3$

Temperature (°C)	n
594	1.74
599	1.70
600	1.55
603	1.56
606	1.64
615	1.40
617	1.32
618	1.29
627	1.21
628	1.13

This variation in the values of n, with the trend to lower values for the isothermal runs at higher temperatures may be due to the fact that the assumption that the praseodymium chromate (V) formed remains stable until all of the chromate (VI) is decomposed is less likely to be justified at higher temperatures where decomposition of chromate (V) to chromate (III) is liable to occur to some extent simultaneously with the decomposition of the chromate (VI). This is further indicated by the fact that for the lower temperature decompositions viz. 594-606°C, the power law gave a reasonable fit only for the first 30% of decomposition while for decompositions in the range 615 - 628°C the power law held for the first 70% of decomposition.

Plots of x against t^n were constructed [Fig. XVII], having gradients k^n, and from these a value for the rate constant at each temperature was calculated and are shown in Table XXI overleaf.

FIG. XVI

POWER LAW APPLIED TO THE DECOMPOSITION OF $Pr_2(CrO_4)_3$ – FIRST STAGE

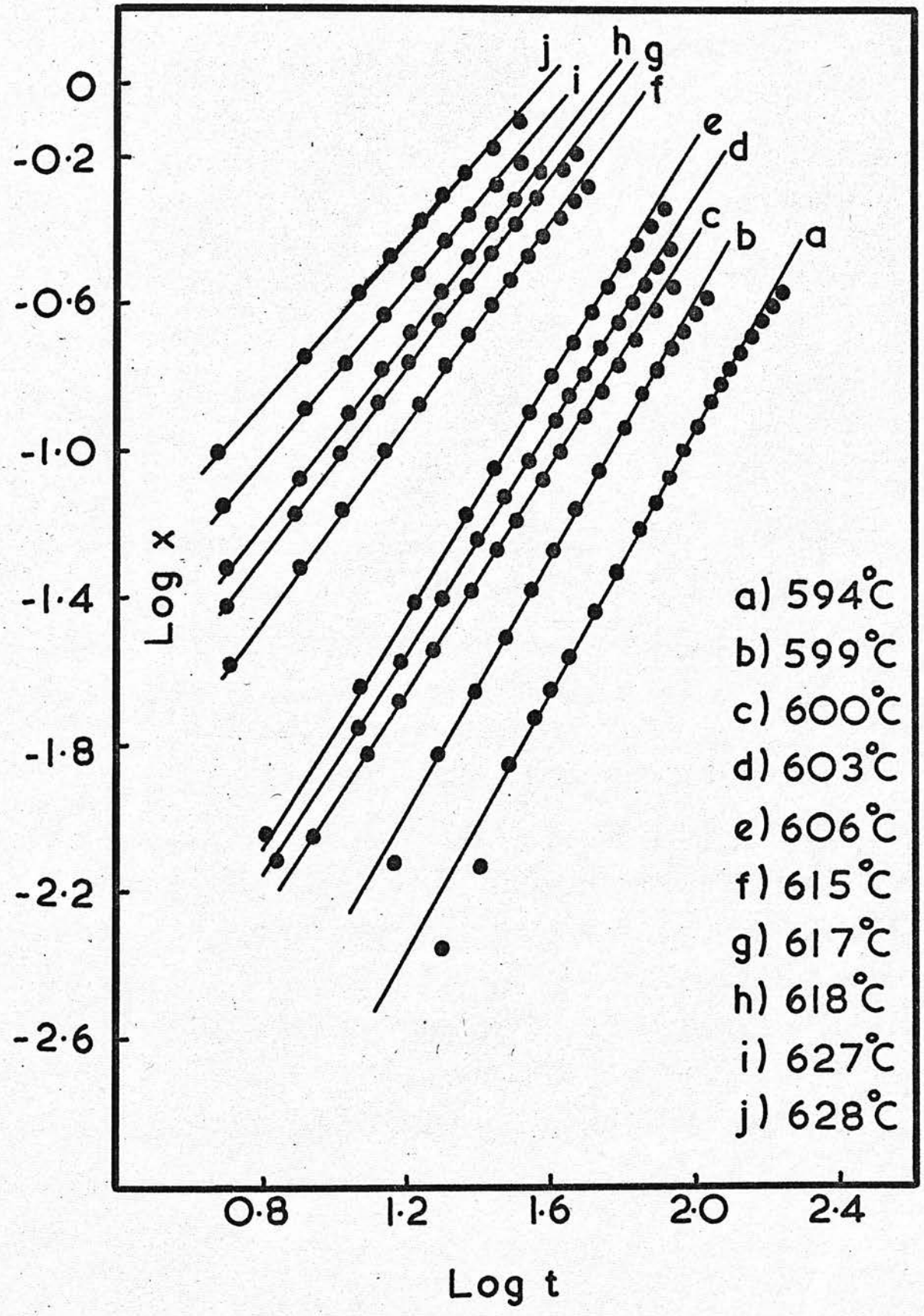


FIG. XVII

POWER LAW APPLIED TO THE DECOMPOSITION OF $Pr_2(CrO_4)_3$ – FIRST STAGE

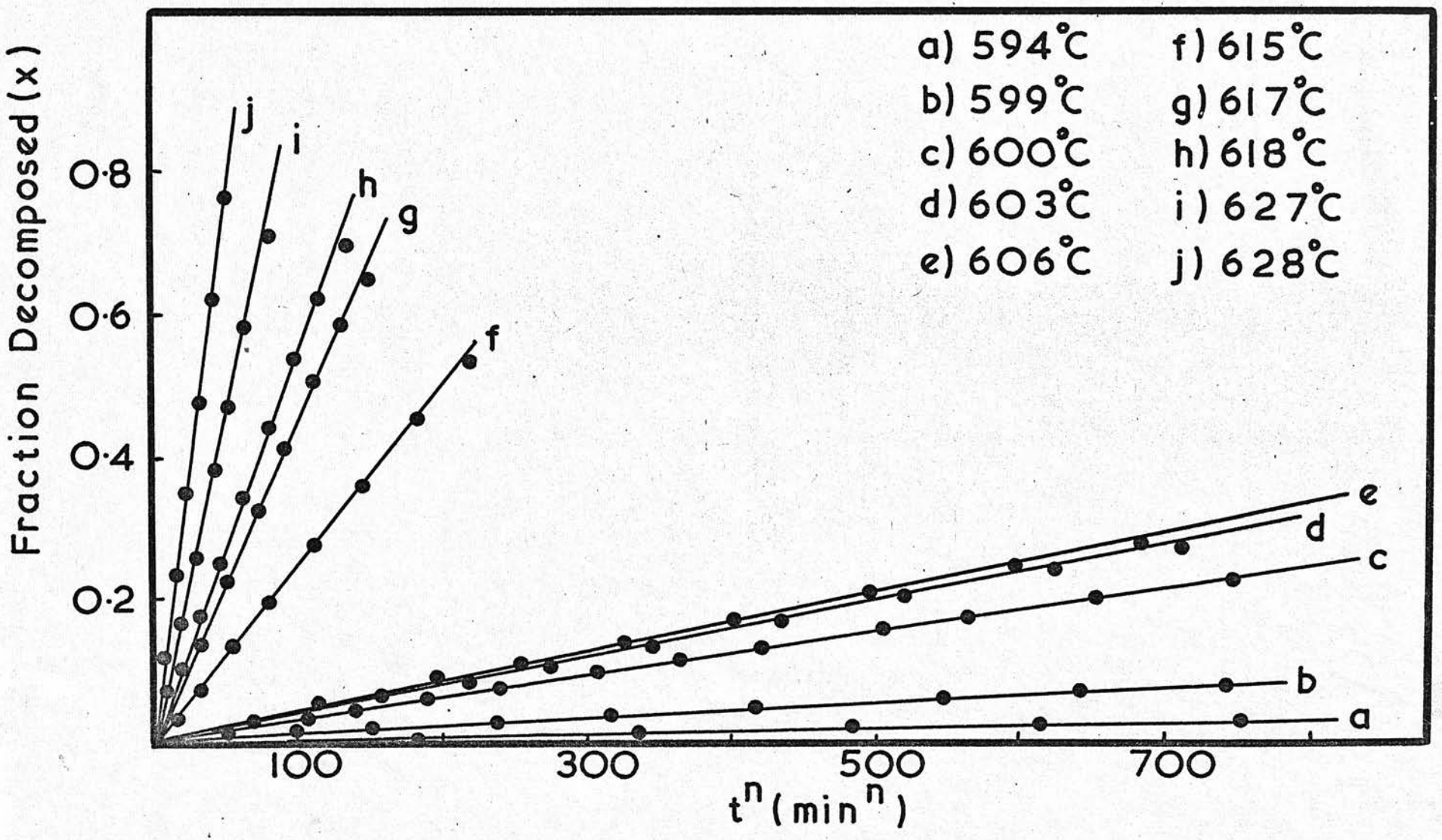


FIG. XVIII

ARRHENIUS PLOT FOR THE POWER LAW APPLIED TO THE FIRST STAGE OF DECOMPOSITION OF $Pr_2(CrO_4)_3$

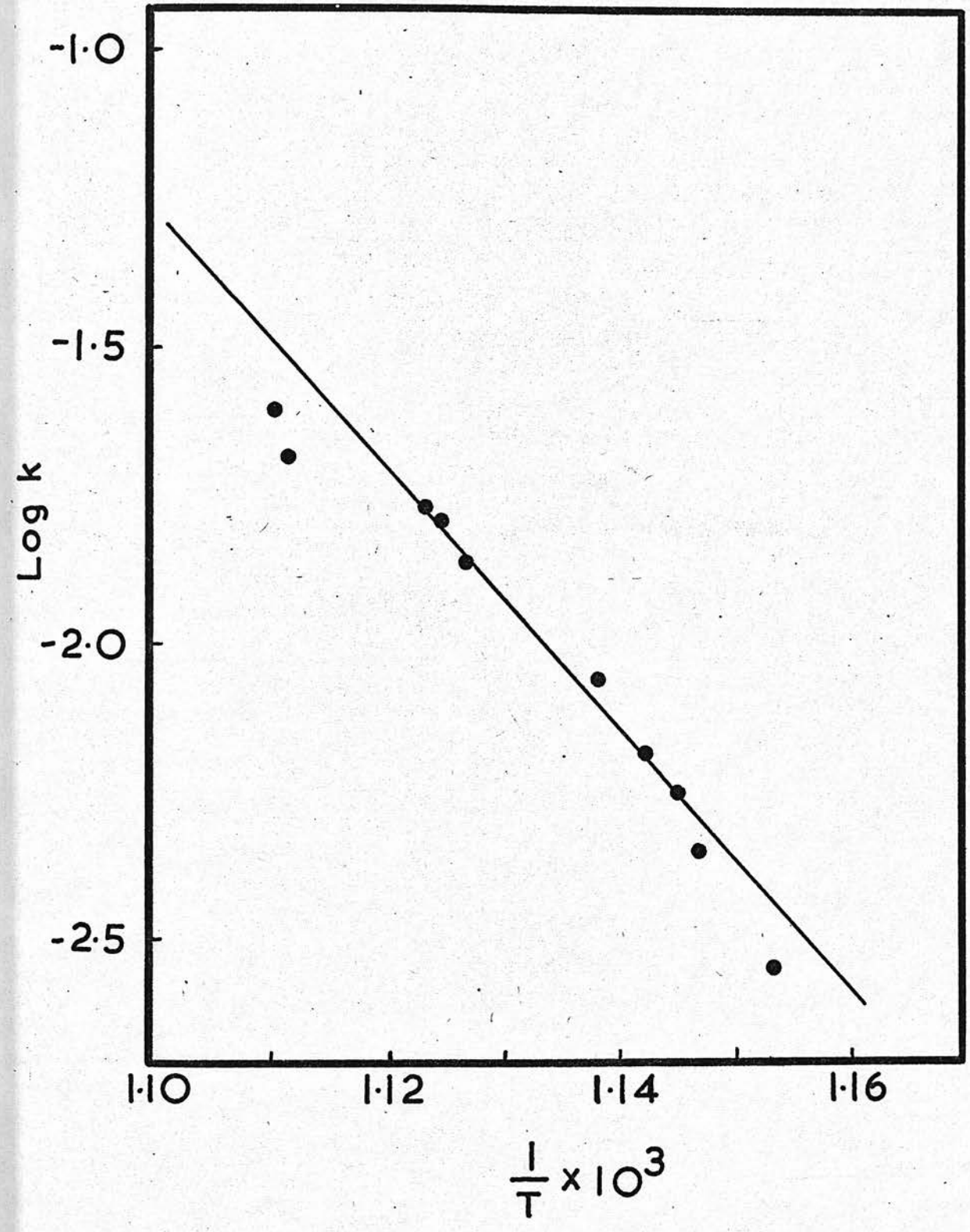


TABLE XXI

RATE CONSTANTS (k) FOR THE POWER LAW APPLIED TO THE FIRST STAGE OF DECOMPOSITION OF $Pr_2(CrO_4)_3$

Absolute Temperature (^oK)	Rate Constant (k) ($mins^{-1}$)
867	(0.0029 ± 0.0003)
872	(0.0044 ± 0.0004)
873	(0.0056 ± 0.0005)
876	(0.0065 ± 0.0006)
879	(0.0087 ± 0.0007)
888	(0.0139 ± 0.0012)
890	(0.0164 ± 0.0014)
891	(0.0172 ± 0.0016)
900	(0.0209 ± 0.0018)
901	(0.0249 ± 0.0020)

These values were then used to construct an Arrhenius plot [Fig. XVIII] and the best line through the experimental points found by a least squares method. From the gradient of this line $\left[-\frac{E}{2.303R}\right]$ the value for the thermal activation energy in the decomposition of praseodymium chromate (VI) was calculated to be 93 ± 17 kcals/mole. The kinetic data for this first stage of decomposition of praseodymium chromate (VI) is given in the Appendix. [Tables A XVIII - A XXVII].

ISOTHERMAL DECOMPOSITIONS OF SOME LANTHANIDE CHROMATES (V)

The isothermal decompositions of the lanthanide chromates (V), the preparations of which were described previously, were studied, using ca. 1.0000 gm. samples, by the thermogravimetric method on the Stanton Mossflow M.F.H.I. automatic recording thermobalance. Care

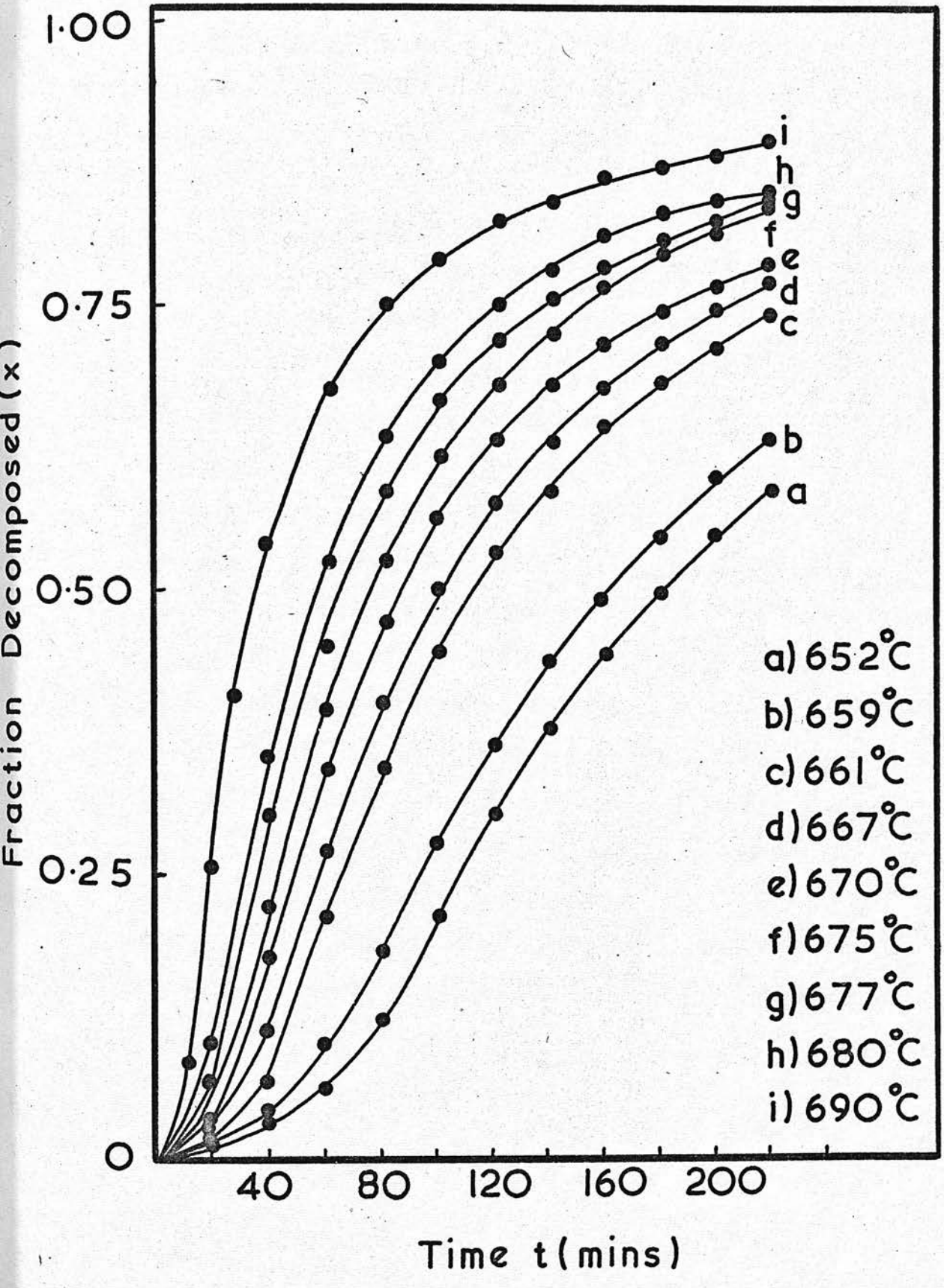
was taken to treat each compound in the same manner so that direct comparisons could be made between the values of thermal activation energies. For each compound, a set of 'x-t' curves was drawn from the isothermal data and the rate laws, mentioned previously, applied to find which laws best fitted the decompositions. It was found that for each compound, there was an initial acceleratory period, which was best fitted by a power law of the type $x = (kt)^n$, which applies for the process of nucleus formation and subsequent growth until appreciable overlap of nuclei occurs. This was followed by a deceleratory period for which two different rate laws gave a reasonable fit. These were:- (a) the first order rate law, $\log \frac{1}{1-x} = kt$, which has previously been reported to apply for many polycrystalline samples [Galwey (1967)]. Reaction of each individual crystal results from the formation of a single nucleus on its surface. The decomposition rate is thus controlled by the nucleation process and since each particle in the assemblage may be nucleated with equal probability, the rate of decomposition obeys first order kinetics, and (b) the contracting plate equation, $1-(1-x)^{\frac{1}{2}} = \frac{k}{a}t$. [Jacobs and Tompkins (1955)]. Each rate law applied was found to fit only a limited range of the decompositions of these chromates (V) and no attempts were made at rate law applications in the range 55-100% decomposition since the regions of primary interest were the activation stages of the decompositions.

Since the same rate laws were found to apply for each compound studied, the decomposition of one compound, erbium chromate (V), will be described in detail and only the results quoted for each of the other compounds.

The isothermal decomposition of erbium chromate (V) was studied in the temperature range 652-690°C and a set of 'x-t' curves constructed [Fig. XIX] using as the value for complete decomposition the

FIG. XIX

FRACTION DECOMPOSED(x) - TIME(t) CURVES FOR THE DECOMPOSITION OF $ErCrO_4$



weight loss calculated from the equation:-

$$ErCrO_4 \longrightarrow ErCrO_3 + 0.5\ O_2$$

A power law in the form $x = (kt)^n$ was applied to those isothermal runs in which the acceleratory period was spread over an appreciable time-span and was found to give a reasonable fit in the range of decomposition $0.03 \leqslant x \leqslant 0.20$. From plots of $\log_{10} x$ against $\log_{10} t$, values of n were calculated [Table XXII] by a least squares method.

TABLE XXII

VALUES OF n FOR POWER LAW APPLIED TO THE DECOMPOSITION OF ERBIUM CHROMATE (V)

Temperature (^oC)	n
652	2.49
659	2.51
661	2.98
667	2.88
670	2.62

Using these values of n, a set of graphs plotting x against t^n was constructed [Fig. XX] and from these a value for the rate constant at each temperature was calculated [Table XXIII] by a least squares method.

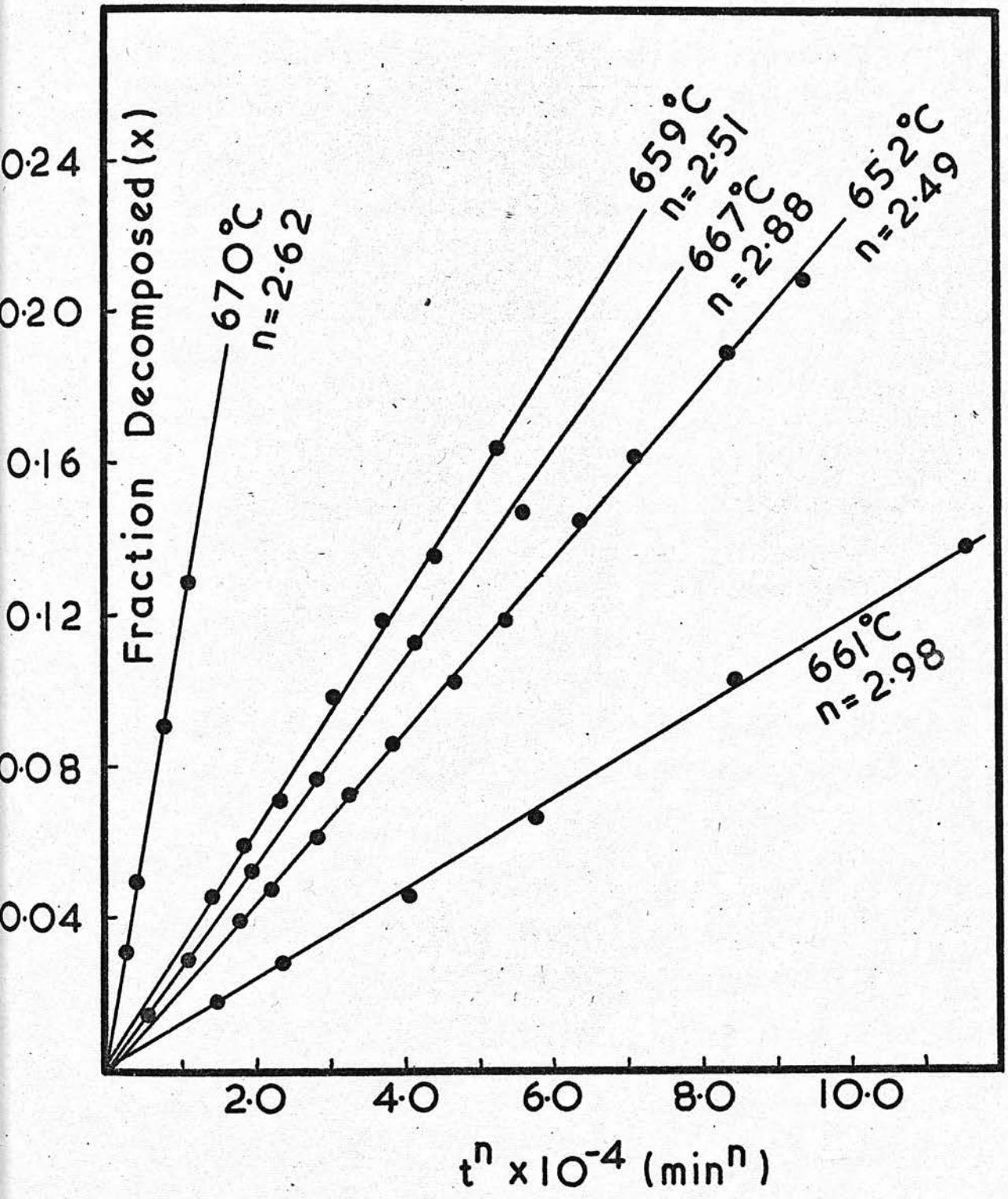
TABLE XXIII

VALUES OF RATE CONSTANTS (k) FOR THE POWER LAW APPLIED TO THE DECOMPOSITION OF ERBIUM CHROMATE (V)

Absolute Temperature (^oK)	Rate Constant k (min^{-1})
925	0.00539 ± 0.00029
932	0.00646 ± 0.00047
934	0.01040 ± 0.00055
940	0.01171 ± 0.00085
943	0.01308 ± 0.00104

FIG. XX

POWER LAW APPLIED TO THE DECOMPOSITION OF $ErCrO_4$



The Arrhenius plot for the power law applied to the decomposition of erbium chromate (V) is shown in Fig. XXIII, and from the gradient of the best straight line through the experimental points a value of thermal activation energy (E) = 89 ± 28 kcals/mole was calculated.

For a limited range of the decay stage of the decomposition of erbium chromate (V), the first order rate law $[0.07 \leq x \leq 0.55]$ and the contracting plate law $[0.05 \leq x \leq 0.45]$ were found to give a reasonable fit [Figs. XXI and XXII]. From these, values of rate constants were again calculated [Table XXIV] and hence, by means of the Arrhenius equation values for the thermal activation energy of the decay stage of the decomposition were obtained [Table XXV]. The Arrhenius plots for the first order rate law and the contracting plate law applied to the decomposition of erbium chromate (V) are shown in Figs. XXIII and XXIV respectively.

TABLE XXIV

VALUES OF RATE CONSTANTS FOR THE DECELERATORY STAGE OF THE DECOMPOSITION OF ERBIUM CHROMATE (V)

Absolute Temperature (^{o}K)	First Order Rate Law k (min^{-1})	Contracting Plate Law $\frac{k}{a}$ (min^{-1})
925	0.00242 ± 0.00022	0.0024 ± 0.0002
932	0.00260 ± 0.00025	0.0026 ± 0.0002
934	0.00380 ± 0.00029	0.0039 ± 0.0003
940	0.00416 ± 0.00032	0.0043 ± 0.0005
943	0.00480 ± 0.00043	0.0047 ± 0.0004
948	0.00552 ± 0.00043	0.0054 ± 0.0005
950	0.00676 ± 0.00059	0.0064 ± 0.0004
953	0.00712 ± 0.00056	0.0070 ± 0.0006
963	0.01080 ± 0.00070	0.0109 ± 0.0008

FIG. XXI

FIRST ORDER LAW APPLIED TO THE DECOMPOSITION OF $ErCrO_4$

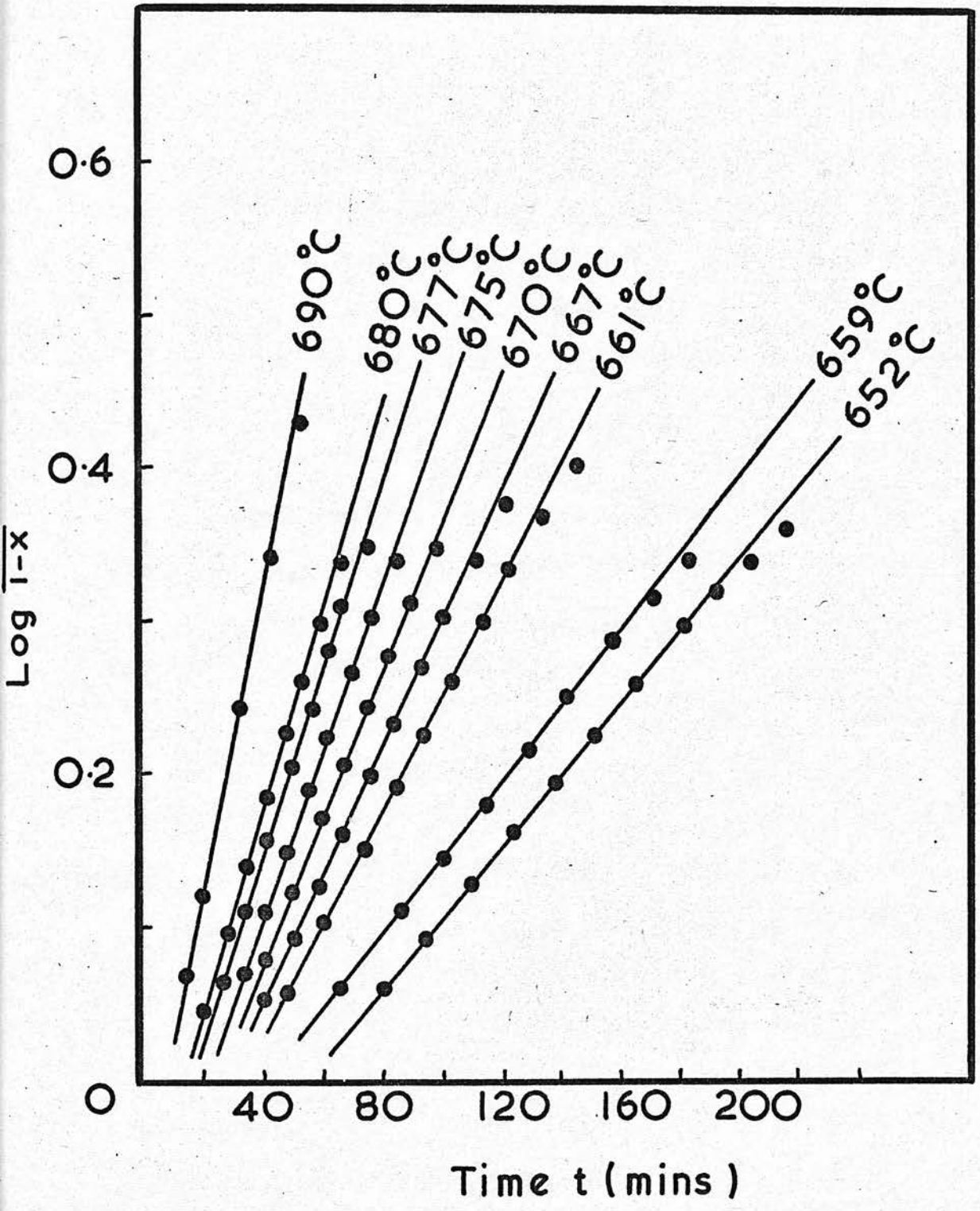


FIG. XXII

CONTRACTING PLATE LAW APPLIED TO THE DECOMPOSITION OF $ErCrO_4$

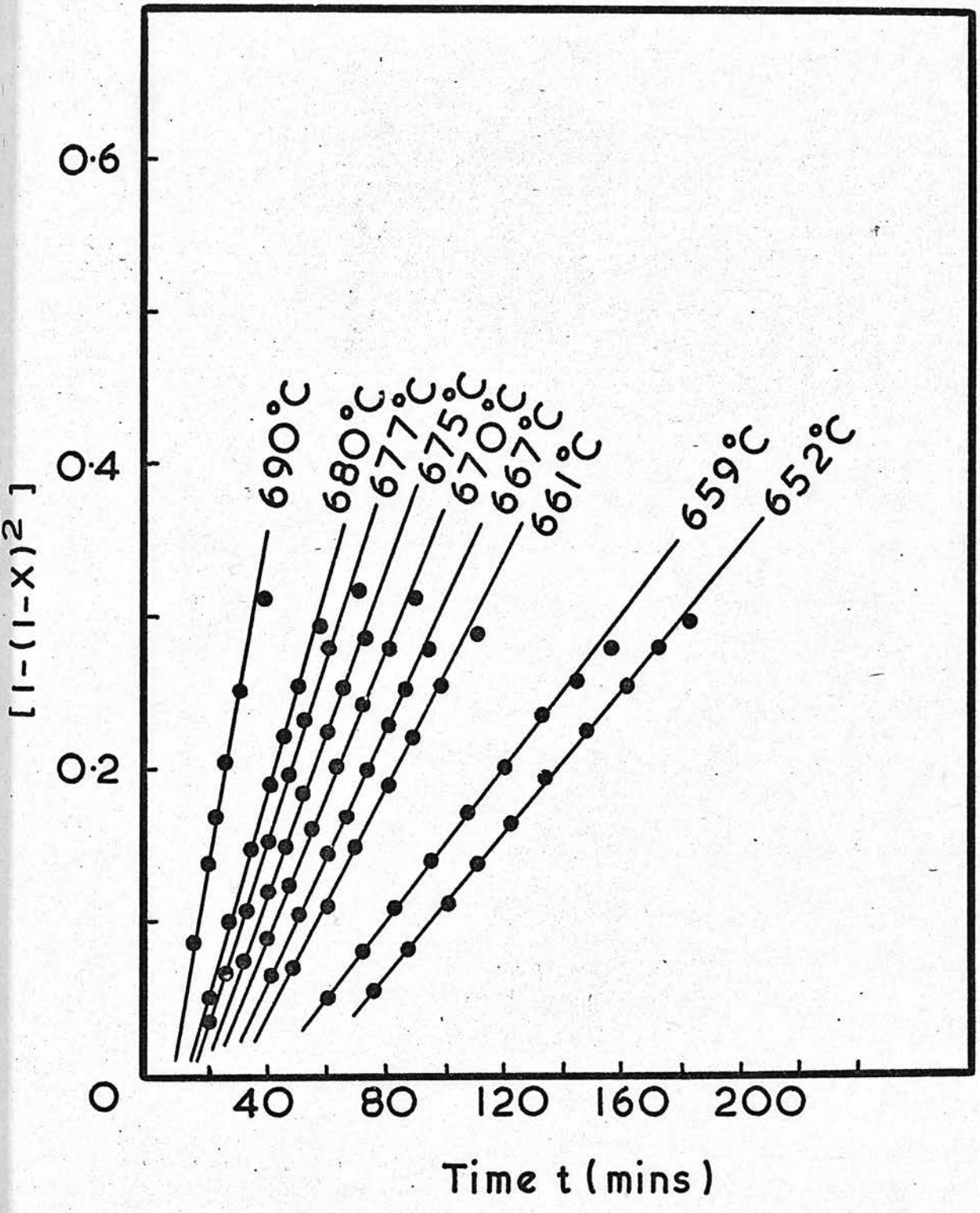


FIG. XXIII

ARRHENIUS PLOTS FOR THE DECOMPOSITION OF $ErCrO_4$

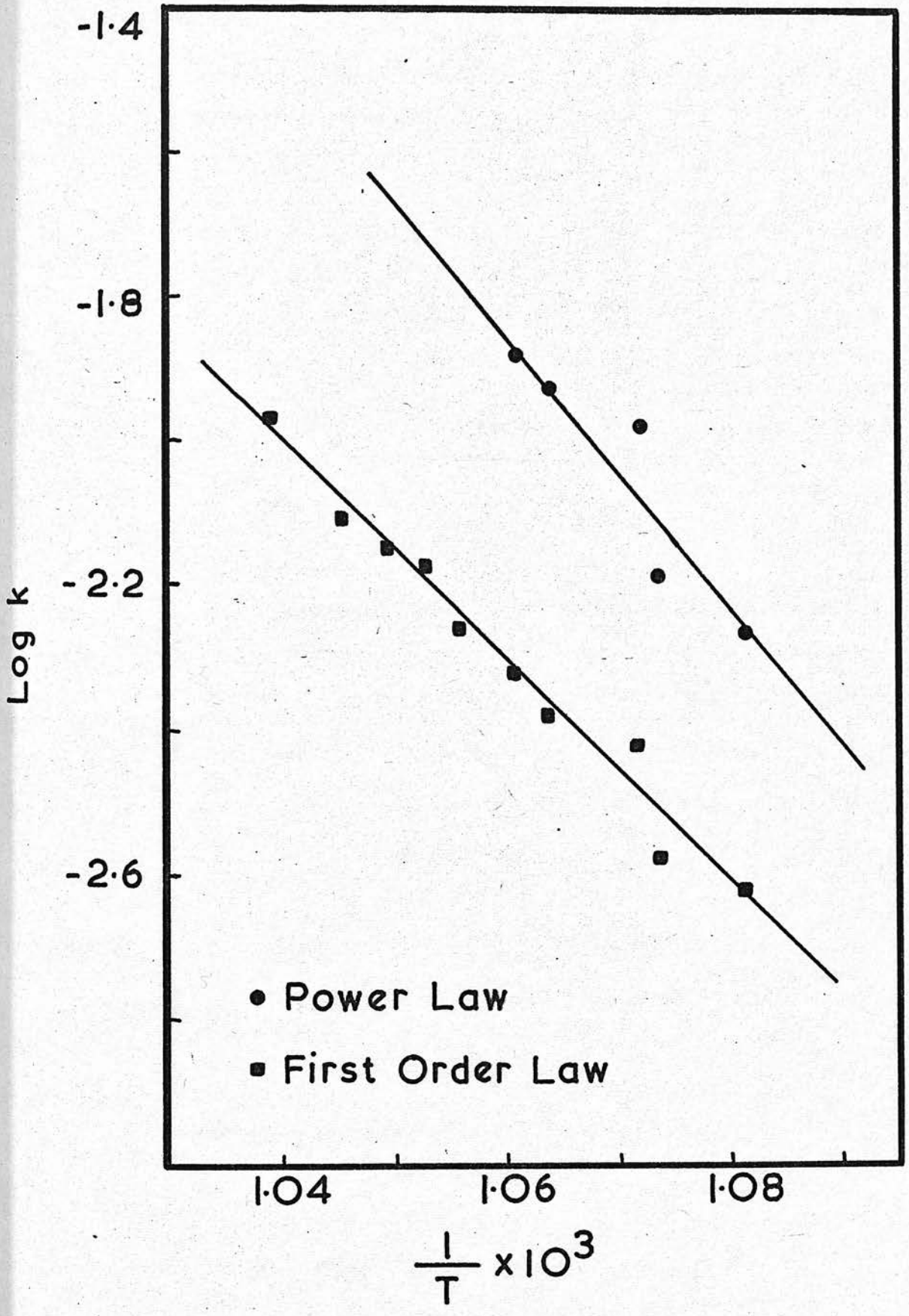


FIG. XXIV

ARRHENIUS PLOT FOR THE CONTRACTING PLATE LAW APPLIED TO THE DECOMPOSITION OF $ErCrO_4$

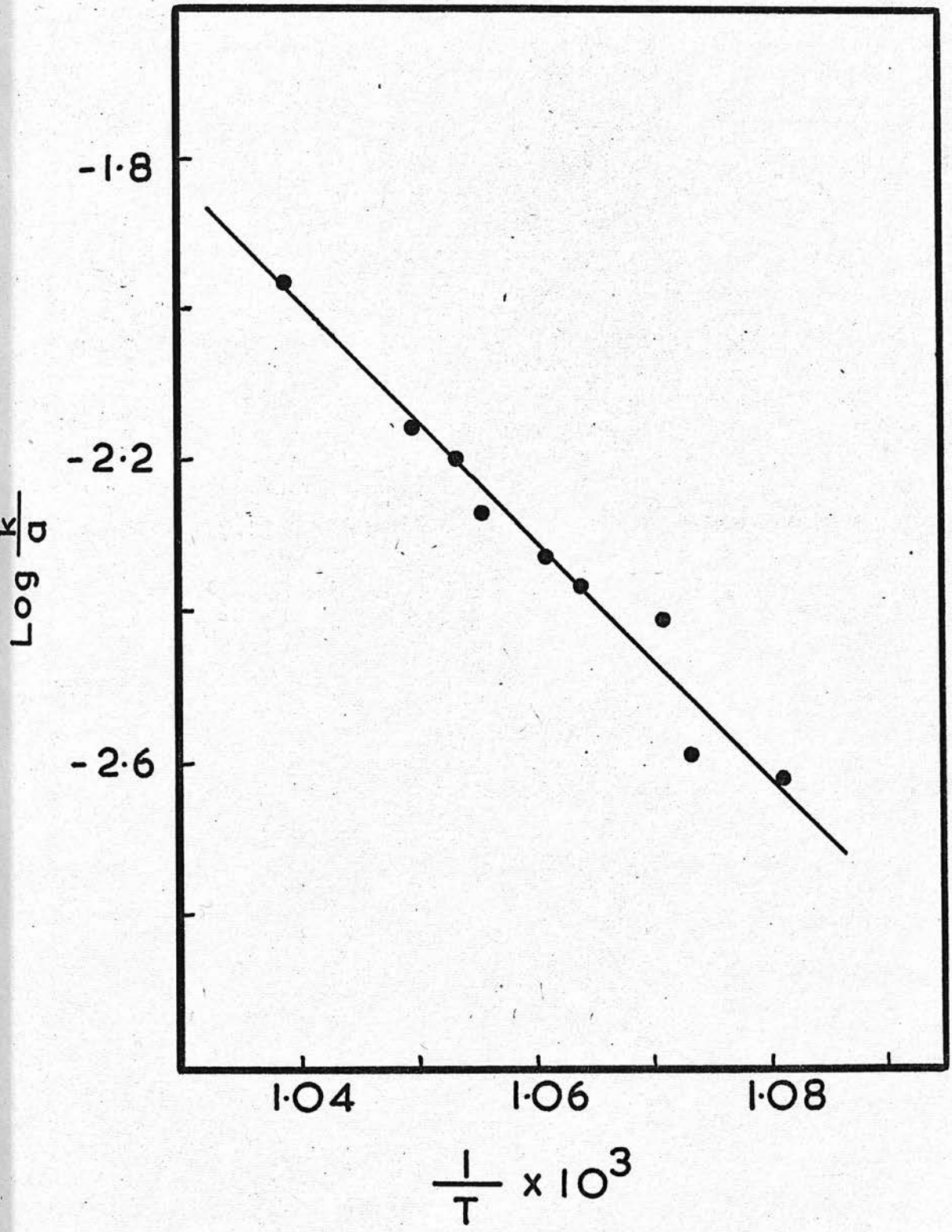


TABLE XXV

SUMMARY OF KINETIC DATA FOR THE

DECOMPOSITION OF ERBIUM CHROMATE (V)

Range Law	Range of Temperature (°C)	Range of x	Activation Energy E (K.cal./mole)
$x = kt^n$	652 - 670	$0.03 \leqslant x \leqslant 0.20$	89 ± 28
$\log_{10} \frac{1}{1-x} = kt$	652 - 690	$0.07 \leqslant x \leqslant 0.55$	72 ± 16
$1-(1-x)^{\frac{1}{2}} = \frac{k}{a}t$	652 - 690	$0.05 \leqslant x \leqslant 0.45$	72 ± 15

The complete kinetic data for the isothermal decompositions of erbium chromate (V) is shown in the Appendix [Tables AL XXIV - AL XXXII]. The kinetic results for the isothermal decompositions of praseodymium chromate (V) are shown in Tables XXVI and XXVII, and the complete kinetic data is shown in the Appendix. [Tables A XXVIII - A XXXVII].

TABLE XXVI

VALUES OF n AND RATE CONSTANTS (k) FOR THE POWER LAW

APPLIED TO THE DECOMPOSITION OF PRASEODYMIUM CHROMATE (V)

Temperature (°K)	n	k (min^{-1})
889	1.29	0.00223 ± 0.00025
895	1.36	0.00294 ± 0.00032
899	1.32	0.00335 ± 0.00034
901	1.34	0.00451 ± 0.00041
903	1.30	0.00462 ± 0.00048
910	1.36	0.00594 ± 0.00056
913	1.32	0.00639 ± 0.00081
914	1.16	0.00889 ± 0.00072
920	1.35	0.01252 ± 0.00095
923	1.29	0.01191 ± 0.00098

TABLE XXVII

VALUES OF RATE CONSTANTS FOR THE DECELERATORY STAGE

OF DECOMPOSITION OF PRASEODYMIUM CHROMATE (V)

Temperature (^{o}K)	First Order Rate Law k (min^{-1})	Contracting Plate Law $\frac{k}{a}$ (min^{-1})
889	0.00124 $\pm$ 0.00013	0.00120 $\pm$ 0.00013
895	0.00154 $\pm$ 0.00018	0.00152 $\pm$ 0.00012
899	0.00175 $\pm$ 0.00019	0.00166 $\pm$ 0.00013
901	0.00256 $\pm$ 0.00025	0.00236 $\pm$ 0.00021
903	0.00256 $\pm$ 0.00027	0.00239 $\pm$ 0.00019
910	0.00312 $\pm$ 0.00028	0.00292 $\pm$ 0.00022
913	0.00383 $\pm$ 0.00035	0.00353 $\pm$ 0.00030
914	0.00533 $\pm$ 0.00049	0.00489 $\pm$ 0.00028
920	0.00669 $\pm$ 0.00049	0.00627 $\pm$ 0.00048
923	0.00656 $\pm$ 0.00050	0.00615 $\pm$ 0.00049

Values of thermal activation energies for the decomposition of praseodymium chromate (V) are shown in Table XXXIX.

The kinetic results for the isothermal decompositions of gadolinium chromate (V) are shown in Table XXVIII and complete kinetic data is shown in the Appendix [Tables A XXXVIII - A XLV].

TABLE XXVIII

VALUES OF RATE CONSTANTS FOR THE DECELERATORY STAGE OF DECOMPOSITION OF GADOLINIUM CHROMATE (V)

Temperature (^{o}K)	First Order Rate Law k (min^{-1})	Contracting Plate Law $\frac{k}{a}$ (min^{-1})
973	0.0060 ± 0.0004	0.0059 ± 0.0005
979	0.0073 ± 0.0005	0.0072 ± 0.0006
984	0.0080 ± 0.0004	0.0085 ± 0.0007
989	0.0119 ± 0.0008	0.0122 ± 0.0010
993	0.0130 ± 0.0008	0.0130 ± 0.0009
996	0.0154 ± 0.0010	0.0159 ± 0.0010
1000	0.0189 ± 0.0013	0.0198 ± 0.0013
1003	0.0198 ± 0.0015	0.0203 ± 0.0015

Values of thermal activation energies for the decomposition of gadolinium chromate (V) are shown in Table XXXIX.

The kinetic results for the isothermal decompositions of terbium chromate (V) are shown in Tables XXIX and XXX and complete kinetic data is shown in the Appendix [Tables A XLVI - A LIII].

TABLE XXIX

VALUES OF n AND RATE CONSTANTS (k) FOR THE POWER LAW APPLIED TO THE DECOMPOSITION OF TERBIUM CHROMATE (V)

Temperature (^{o}K)	n	k (min^{-1})
914	3.13	0.00435 ± 0.00039
920	3.29	0.00519 ± 0.00027
923	2.80	0.00615 ± 0.00032
929	3.21	0.00827 ± 0.00039
931	2.87	0.01169 ± 0.00083

TABLE XXX

VALUES OF RATE CONSTANTS FOR THE DECELERATORY STAGE OF DECOMPOSITION OF TERBIUM CHROMATE (V)

Temperature (^{o}K)	First Order Rate Law k (min^{-1})	Contracting Plate Law $\frac{k}{a}$ (min^{-1})
914	0.00211 ± 0.00019	0.00198 ± 0.00017
920	0.00256 ± 0.00022	0.00238 ± 0.00020
923	0.00304 ± 0.00026	0.00295 ± 0.00027
929	0.00371 ± 0.00032	0.00356 ± 0.00026
931	0.00527 ± 0.00041	0.00531 ± 0.00048
940	0.00619 ± 0.00049	0.00611 ± 0.00025
946	0.01042 ± 0.00071	0.01024 ± 0.00067
955	0.01655 ± 0.00109	0.01567 ± 0.00096

Values of thermal activation energies for the decomposition of terbium chromate (V) are shown in Table XXXIX.

The kinetic results for the isothermal decompositions of dysprosium chromate (V) are shown in Tables XXXI and XXXII and complete kinetic data is shown in the Appendix [Tables A LIV - A LXIII].

TABLE XXXI

VALUES OF n AND RATE CONSTANTS (k) FOR THE POWER LAW APPLIED TO THE DECOMPOSITION OF DYSPROSIUM CHROMATE (V)

Temperature (^{o}K)	n	k (min^{-1})
908	2.40	0.00305 ± 0.00013
911	2.77	0.00451 ± 0.00025
914	2.77	0.00520 ± 0.00036
917	3.32	0.00592 ± 0.00030
919	2.92	0.00625 ± 0.00042
921	2.97	0.00804 ± 0.00048
923	3.36	0.00976 ± 0.00056

TABLE XXXII

VALUES OF RATE CONSTANTS FOR THE DECELERATORY STAGE OF DECOMPOSITION OF DYSPROSIUM CHROMATE (V)

Temperature (^{o}K)	First Order Rate Law k (min^{-1})	Contracting Plate Law $\frac{k}{a}$ (min^{-1})
908	0.00176 ± 0.00022	0.00169 ± 0.00020
911	0.00203 ± 0.00017	0.00203 ± 0.00020
914	0.00229 ± 0.00020	0.00217 ± 0.00019
917	0.00251 ± 0.00022	0.00250 ± 0.00023
919	0.00278 ± 0.00022	0.00268 ± 0.00022
921	0.00347 ± 0.00022	0.00342 ± 0.00029
923	0.00380 ± 0.00040	0.00364 ± 0.00031
928	0.00421 ± 0.00034	0.00431 ± 0.00047
933	0.00516 ± 0.00040	0.00533 ± 0.00048
945	0.01048 ± 0.00093	0.01041 ± 0.00092

Values of thermal activation energies for the decomposition of dysprosium chromate (V) are shown in Table XXXIX.

The kinetic results for the isothermal decompositions of holmium chromate (V) are shown in Tables XXXIII and XXXIV and complete kinetic data is shown in the Appendix [Tables A LXIV - A LXXIII].

TABLE XXXIII

VALUES OF n AND RATE CONSTANTS (k) FOR THE POWER LAW APPLIED TO THE DECOMPOSITION OF HOLMIUM CHROMATE (V)

Temperature (^{o}K)	n	k (min^{-1})
922	3.07	0.00378 ± 0.00024
928	2.61	0.00543 ± 0.00029
933	2.82	0.00594 ± 0.00036
935	2.95	0.00755 ± 0.00038
938	3.03	0.00896 ± 0.00045
941	2.48	0.01302 ± 0.00082

TABLE XXXIV

VALUES OF RATE CONSTANTS FOR THE DECELERATORY STAGE OF DECOMPOSITION OF HOLMIUM CHROMATE (V)

Temperature (^{o}K)	First Order Rate Law k (min^{-1})	Contracting Plate Law $\frac{k}{a}$ (min^{-1})
922	0.0014 ± 0.0002	0.0014 ± 0.0001
928	0.0023 ± 0.0002	0.0023 ± 0.0003
933	0.0023 ± 0.0003	0.0023 ± 0.0002
935	0.0029 ± 0.0003	0.0029 ± 0.0002
938	0.0035 ± 0.0003	0.0036 ± 0.0004
941	0.0048 ± 0.0005	0.0049 ± 0.0005
943	0.0051 ± 0.0004	0.0053 ± 0.0004
948	0.0056 ± 0.0004	0.0059 ± 0.0005
953	0.0073 ± 0.0005	0.0077 ± 0.0008
959	0.0081 ± 0.0007	0.0083 ± 0.0009

Values of thermal activation energies for the decomposition of holmium chromate (V) are shown in Table XXXIX.

The kinetic results for the isothermal decompositions of ytterbium chromate (V) are shown in Tables XXXV and XXXVI and complete kinetic data is shown in the Appendix [Tables A LXXXIII - A XCII].

TABLE XXXV

VALUES OF n AND RATE CONSTANTS (k) FOR THE POWER LAW APPLIED TO THE DECOMPOSITION OF YTTERBIUM CHROMATE (V)

Temperature (^{o}K)	n	k (min^{-1})
901	3.23	0.00236 $\pm$ 0.00015
907	2.88	0.00365 $\pm$ 0.00020
910	2.57	0.00384 $\pm$ 0.00023
914	2.81	0.00513 $\pm$ 0.00033
920	2.86	0.00633 $\pm$ 0.00045
923	2.46	0.00769 $\pm$ 0.00048
925	2.67	0.00829 $\pm$ 0.00069
927	2.86	0.00954 $\pm$ 0.00078
934	2.87	0.01217 $\pm$ 0.00069
943	2.50	0.01503 $\pm$ 0.00094

TABLE XXXVI

VALUES OF RATE CONSTANTS FOR THE DECELERATORY STAGE OF DECOMPOSITION OF YTTERBIUM CHROMATE (V)

Temperature (^{o}K)	First Order Rate Law k (min^{-1})	Contracting Plate Law $\frac{k}{a}$ (min^{-1})
907	0.00195 $\pm$ 0.00021	0.00186 $\pm$ 0.00019
910	0.00222 $\pm$ 0.00025	0.00199 $\pm$ 0.00020
914	0.00267 $\pm$ 0.00026	0.00250 $\pm$ 0.00023
920	0.00292 $\pm$ 0.00027	0.00272 $\pm$ 0.00025
923	0.00425 $\pm$ 0.00039	0.00388 $\pm$ 0.00039
925	0.00420 $\pm$ 0.00043	0.00391 $\pm$ 0.00038
927	0.00428 $\pm$ 0.00038	0.00407 $\pm$ 0.00036
934	0.00586 $\pm$ 0.00054	0.00525 $\pm$ 0.00038
943	0.00755 $\pm$ 0.00054	0.00712 $\pm$ 0.00059

Values of the thermal activation energies for the decomposition of ytterbium chromate (V) are shown in Table XXXIX.

The kinetic results for the isothermal decompositions of yttrium chromate (V) are shown in Tables XXXVII and XXXVIII and complete kinetic data is shown in the Appendix [Tables A XCIII - A CI].

TABLE XXXVII

VALUES OF n AND RATE CONSTANTS (k) FOR THE POWER LAW APPLIED TO THE DECOMPOSITION OF YTTRIUM CHROMATE (V)

Temperature (^{o}K)	n	k (min^{-1})
924	2.70	0.00285 $\pm$ 0.00011
929	2.54	0.00309 $\pm$ 0.00011
931	2.61	0.00362 $\pm$ 0.00015
933	2.76	0.00507 $\pm$ 0.00020
935	3.22	0.00645 $\pm$ 0.00041
938	3.13	0.00717 $\pm$ 0.00025
943	3.12	0.00975 $\pm$ 0.00046

TABLE XXXVIII

VALUES OF RATE CONSTANTS FOR THE DECELERATORY STAGE OF THE DECOMPOSITION OF YTTRIUM CHROMATE (V)

Temperature (^{o}K)	First Order Rate Law k (min^{-1})	Contracting Plate Law $\frac{k}{a}$ (min^{-1})
924	0.0014 ± 0.0002	0.0014 ± 0.0002
929	0.0017 ± 0.0002	0.0017 ± 0.0001
931	0.0021 ± 0.0002	0.0019 ± 0.0001
933	0.0026 ± 0.0002	0.0025 ± 0.0002
935	0.0029 ± 0.0002	0.0028 ± 0.0002
938	0.0034 ± 0.0002	0.0033 ± 0.0003
943	0.0044 ± 0.0003	0.0043 ± 0.0003
953	0.0058 ± 0.0004	0.0056 ± 0.0003
974	0.0128 ± 0.0007	0.0126 ± 0.0006

Values of the thermal activation energies for the decomposition of yttrium chromate (V) are shown in Table XXXIX.

TABLE XXXIX

THERMAL ACTIVATION ENERGIES (E) FOR THE DECOMPOSITIONS

OF SOME LANTHANIDE CHROMATES (V)

Compound	RATE LAWS					
	Power Law		First Order Law		Contracting Plate Law	
	Range of x	E (kcals/mole)	Range of x	E (kcals/mole)	Range of x	E (kcals/mole)
$PrCrO_4$	$0.05 \leq x \leq 0.27$	85 ± 22	$0.15 \leq x \leq 0.50$	86 ± 22	$0.15 \leq x \leq 0.50$	84 ± 20
$GdCrO_4$	-	-	$0.05 \leq x \leq 0.50$	83 ± 10	$0.05 \leq x \leq 0.45$	85 ± 11
$TbCrO_4$	$0.01 \leq x \leq 0.17$	93 ± 30	$0.10 \leq x \leq 0.50$	88 ± 16	$0.10 \leq x \leq 0.50$	89 ± 15
$DyCrO_4$	$0.02 \leq x \leq 0.20$	114 ± 43	$0.10 \leq x \leq 0.50$	80 ± 18	$0.10 \leq x \leq 0.45$	83 ± 19
$HoCrO_4$	$0.02 \leq x \leq 0.20$	104 ± 32	$0.10 \leq x \leq 0.45$	88 ± 16	$0.06 \leq x \leq 0.40$	82 ± 12
$ErCrO_4$	$0.03 \leq x \leq 0.20$	89 ± 28	$0.07 \leq x \leq 0.55$	72 ± 16	$0.05 \leq x \leq 0.45$	72 ± 15
$YbCrO_4$	$0.05 \leq x \leq 0.20$	76 ± 13	$0.19 \leq x \leq 0.55$	66 ± 17	$0.15 \leq x \leq 0.50$	65 ± 17
$YCrO_4$	$0.02 \leq x \leq 0.20$	125 ± 27	$0.15 \leq x \leq 0.50$	78 ± 13	$0.10 \leq x \leq 0.45$	79 ± 11

These values of thermal activation energies Table XXXIX will be discussed later in connection with the mechanism of decomposition of the lanthanide chromates (V).

PHYSICAL MEASUREMENTS ON DECOMPOSED SAMPLES OF CHROMATES (V) AND PRASEODYMIUM CHROMATE (VI)

X-ray diffraction patterns, infrared absorption spectra and magnetic susceptibilities were recorded for partially and completely decomposed samples of some chromates (V) and praseodymium chromate (VI) and compared with the equivalent measurements recorded for the undecomposed materials and the individual decomposition products in an attempt to identify any intermediates formed during the course of decompositions.

The detection of decomposition intermediates was of primary interest in the decomposition of praseodymium chromate (VI) where, as stated earlier, difficulty was encountered in identifying a chromate (V) intermediate by means of e.s.r. spectroscopy. A previous investigation [Schwarz (1963)] indicated, that some of the lines from X-ray diffraction patterns of partially decomposed samples of praseodymium chromate (VI) could be assigned to praseodymium chromate (V). A similar investigation has been carried out in the present work and the results are shown in Table XL. These results show the disappearance of the lines due to the praseodymium chromate (VI), none of which could be observed when decomposition had proceeded beyond 40%, and the appearance of other lines, some of which could be assigned to the zirconite or Huttonite reflections of praseodymium chromate (V) and others to the final decomposition product, praseodymium chromate (III). No lines assignable to the other end product, chromium (III) oxide, were observed, but this would be present only in fairly low concentration.

TABLE XL

X-RAY DIFFRACTION RESULTS FOR DECOMPOSITION PRODUCTS

OF PRASEODYMIUM CHROMATE (VI)

$Pr_2(CrO_4)_3$		x = 0.38		$Pr\ CrO_4$			x = 0.47		x = 0.59		x = 0.84		$Pr\ CrO_3$	
dÅ	Int.	dÅ	Int.	dÅ	Int.	$dÅ_H$*	dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.
6.51	85													
5.37	77													
				4.87	37		4.80	21	4.77	25				
						4.33								
									3.82	16	3.87	30	3.85	18
		3.71	100	3.69	100		3.66	100	3.63	99	3.66	22		
3.62	73													
						3.55								
				3.36	26	3.35	3.33	8						
				3.16	29	3.16								
3.05	100					3.04	2.99	14						
				2.931	43	2.903	2.912	10						
2.858	75													

Contd.....

TABLE XL (Contd.)

$Pr_2(CrO_4)_3$		x = 0.38		Pr CrO_4			x = 0.47		x = 0.59		x = 0.84		Pr CrO_3	
dÅ	Int.	dÅ	Int.	dÅ	Int.	d_HÅ*	dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.
		2.732	50				2.722	69	2.716	100	2.730	100	2.722	100
		2.607	25	2.600	26	26								
							2.585	45	2.578	22			2.571	7
2.488	48													
													2.327	8
		2.298	21	2.293	26									
						2.238								
									2.212	18	2.233	19	2.222	22
						2.206								
													2.141	10
						1.981								
		1.945	20	1.945	23	1.941	1.937	12						
											1.926	36	1.929	37
						1.918								
				1.880	33	1.888	1.876	55	1.870	53				
											1.873	11	1.873	12

* Reference:- Huttonite reflections quoted by Schwarz (1963)

As shown in Table XL, the major product formed during the initial stage of decomposition of praseodymium chromate (VI) $[x < 0.50]$ is praseodymium chromate (V) but some further decomposition to praseodymium chromate (III) also occurs during this period. This invalidates to some extent the assumption made in the kinetic studies that the two stages of decomposition occur independently, although it would appear that for at least the first 30% of decomposition such an assumption could be considered justified. The later stage of decomposition $[x > 0.50]$ is seen to involve the subsequent decomposition, to praseodymium chromate (III), of the praseodymium chromate (V) formed initially.

A comparison of the infrared absorption maxima of some partially decomposed samples with those of praseodymium chromates (VI), (V) and (III) is shown in Table A CII of the Appendix. It is rather more difficult to draw definite conclusions from this evidence, due to the width of the absorptions, but it is significant that the strongest absorption in the spectrum of praseodymium chromate (III) was not observed for partially decomposed samples of chromate (VI) where percentage decomposition was less than 50%. This alone would seem to indicate that the chromate (III) is not the major product formed initially.

The results of magnetic susceptibility measurements on partially decomposed samples of praseodymium chromate (VI) are shown in Table XLI. The values show the expected trend with increasing value of percentage decomposition, but no information regarding the exact compositions of the samples was obtained.

TABLE XLI

MAGNETIC MEASUREMENTS ON PARTIALLY DECOMPOSED SAMPLES OF PRASEODYMIUM CHROMATE (VI)

Sample	Temp. (°C)	Susceptibility /gm. ($X10^6$) c.g.s. units
$Pr_2(CrO_4)_3$	19.0	16.84
x = 0.38	18.0	17.26
$Pr\ CrO_4$	19.0	23.96
x = 0.73	19.7	24.86
x = 0.84	19.5	26.17
$Pr\ CrO_3$	19.0	28.51

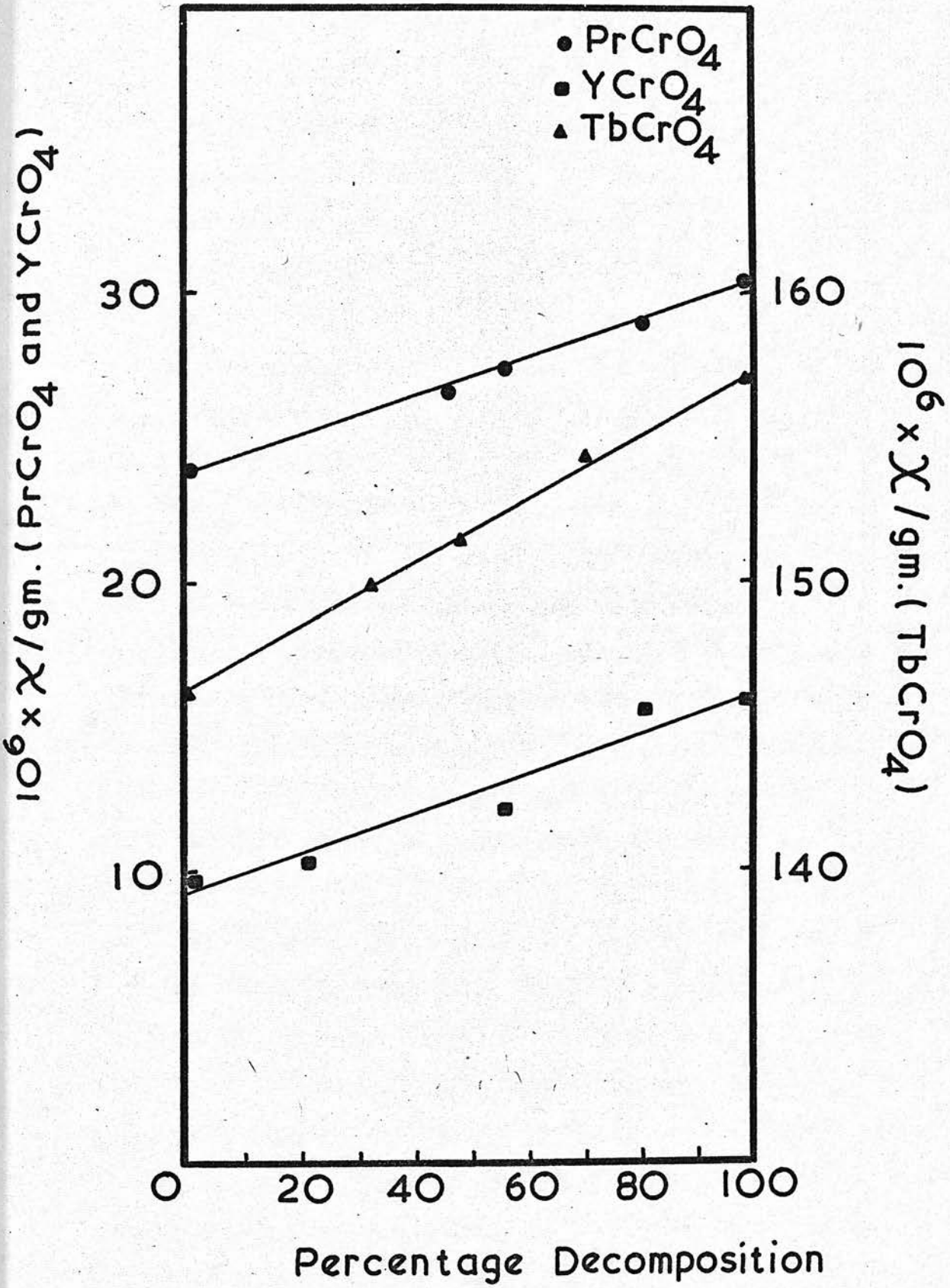
The X-ray diffraction patterns of partially decomposed samples of some lanthanide chromates (V) are shown in Tables A CIII - A CX of the Appendix. No reaction intermediates were observed from these, only the disappearance of lines due to the chromates (V) and corresponding appearance of lines due to the chromates (III).

A similar situation was found from the infrared spectra of these partially decomposed samples of the lanthanide chromates (V) [see Appendix Tables A CXI - A CXVIII], with all absorptions assignable to either the parent chromate (V) compound or the chromate (III) product.

On examination of the magnetic susceptibilities of some of the partially and completely decomposed samples of lanthanide chromates (V), the changes in susceptibilities with increase in percentage decomposition were not always found to be regular, although the relationship between measured percentage decomposition and magnetic susceptibility appears to be linear. [Fig. XXV]. The reason for the variations in values of magnetic susceptibilities is

FIG. XXV

VARIATION OF MAGNETIC SUSCEPTIBILITY WITH PERCENTAGE DECOMPOSITION FOR SOME CHROMATES(V)



thought to be the failure to obtain consistently good packing of the samples in the Gouy tube because of the rather small quantities of material available in some cases. Magnetic measurements on the lanthanide chromates (III) and the partially decomposed chromates (V) were liable to greater error than measurements on the lanthanide chromates (V) since the antiferromagnetism shown by the chromates (III) made measurements impractical at all magnetic field settings other than the lowest one. Instead of these values being the mean of five separate measurements, many of them have been calculated from only a single measurement. Of the chromates (V) studied, only those of praseodymium and yttrium showed a sufficiently good linear relationship between magnetic susceptibility and measured percentage decomposition to be used in further calculations.

In a previous investigation [Darrie (1967)], the measured magnetic susceptibilities of partially decomposed samples of the chromates (V) of lanthanum, samarium and neodymium were applied to the following equation:-

$$(1-x)\chi_{RCrO_4} = \frac{(M_{(RCrO_3)})}{(M_{(RCrO_4)})}x\,\chi_{RCrO_3} = (1-\frac{M(O_2)}{2M_{(RCrO_4)}})\,\chi_{\text{mixture}}$$

where x = fractional decomposition; χ = susceptibility /gm; R = lanthanide ion; M = molecular weight. Values of percentage decompositions calculated by this means were compared with the values found thermogravimetrically. The agreement found in this previous work was generally rather poor and likewise in the present work, the results shown for the chromates (V) of praseodymium and yttrium [Tables XLII and XLIII] give fairly poor agreement.

TABLE XLII

MAGNETIC SUSCEPTIBILITIES OF DECOMPOSED SAMPLES

OF PRASEODYMIUM CHROMATE (V)

Magnetic Susceptibility /gm x 10^6	Calculated % Decomp.	Measured % Decomp.
26.69	38.0	45.0
27.52	49.0	55.0
28.96	68.0	80.0
30.49	87.0	100.0

TABLE XLIII

MAGNETIC SUSCEPTIBILITIES OF DECOMPOSED SAMPLES

OF YTTRIUM CHROMATE (V)

Magnetic Susceptibility /gm x 10^6	Calculated % Decomp.	Measured % Decomp.
9.94	38.0	32.0
11.49	53.0	48.0
14.40	80.0	70.0
17.03	103.0	100.0

The conclusions that may be drawn from these magnetic susceptibility measurements are:- (a) The magnetic susceptibility is directly proportional to the percentage decomposition. (b) The susceptibilities of the individual components of each mixture are additive. These conclusions however, must be rather tentative, since practical considerations lead to certain inaccuracies in the susceptibility measurements.

DISCUSSION

The kinetic results from the thermal decompositions of the lanthanide chromates (V) and praseodymium chromate (VI) are now discussed with a view to proposing a mechanism for the activation processes in the decomposition.

The decomposition of praseodymium chromate (VI) has been shown to have an initial acceleratory period, which obeyed a power law of the type $x = kt^n$, followed by a deceleratory period. The values of n for the acceleratory period were in the range 1.10 - 1.75 and powers of n in the range 1 - 2 were interpreted by Yankwich and Zavitsanos (1964) as indicating more than one nucleation - growth process occurring during the acceleratory phase. This acceleratory period is likely to correspond to initial surface decomposition leading to the setting up of reactant/product interfaces which will then progress into the particles.

A mechanism has been proposed [Darrie et al. (1967)] for the decomposition of some lanthanide chromates (VI) in which the activation process is thought to be a single electron transfer from co-ordinated oxygen to chromium within the chromate (VI) group. The energy of this electron transfer process is measured by the energy of the $t_1 \rightarrow 2e$ charge transfer band in the chromate (VI) spectrum. A comparison of the energy of this first charge transfer band in the spectrum with the thermal activation energy found for the decomposition of praseodymium chromate (VI) is shown below:-

	Thermal Activation Energy (cm^{-1})	Energy of $t_1 \rightarrow 2e$ Transition (cm^{-1})
$Pr_2(CrO_4)_3$	$32,500 \pm 5,900$	28,400

The agreement found here, within the limits of experimental error, is further indication that the proposed mechanism is correct. It was further suggested [Darrie et. al. (1967)] that the reason for these lanthanide chromates (VI) decomposing in the temperature range 500 - 700°C while some other chromates (VI) (e.g. those of the alkali and alkaline earth metals) are much more thermally stable, is due to structural differences. The crystal structures of these lanthanide chromates (VI) are unknown; but from evidence in the infrared spectra of anion-anion coupling and the fact that they decompose in the same temperature range as magnesium chromate (VI) which has the $CrVO_4$ structure [Brandt (1943)], in which there are chains of chromate (VI) tetrahedra, it was suggested that these compounds also have chains of chromate (VI) tetrahedra in their structure. In chromates (VI) with this type of structure, the activation process will be readily transmitted to the surface, along the chains of tetrahedra, while in chromates (VI) of the alkali and alkaline earth metals, the anions are separated by the cations and propagation in this way is not possible.

There are three mechanisms for energy transfer in compounds of this type, which may be applicable:-

1) Transfer by means of interaction of dipole fields.

2) Transfer by dipole - quadrupole interaction.

3) Transfer by exchange.

The mechanism of energy transfer in these lanthanide chromates (VI) is likely to be by the short range exchange mechanism, since the low oscillator strength of the chromate (VI) group absorption, 0.089 [Wolfsberg and Helmholtz (1952)], makes transfer by either mechanism (1) or (2) unlikely. The probability of energy transfer by an

exchange mechanism can be written as a product of two terms [Blasse and Bril (1966)]:- one connected with the orbital overlap integral of the centres and the other with the energy overlap of the emission and absorption bands of the anion (where exchange is occurring between identical anions). No information is available on the emission levels of the chromate (VI) group, but in general there is usually a certain amount of overlap between the absorption and emission bands of an anion. Since there is evidence of fairly strong anion-anion coupling in these compounds, the degree of orbital overlap between neighbouring chromate (VI) groups should be sufficiently good to allow energy transfer by exchange to occur quite readily.

The results obtained for the decomposition of the lanthanide chromates (V) studied in this work are now discussed, and for completeness, the results found by Darrie (1967) for the chromates (V) of lanthanum, samarium and neodymium are also considered. In the decomposition of each chromate (V), there is an initial acceleratory period, following a power law ($x = kt^n$), with all values of n being in the range 1 - 3.5, indicating that more than one nucleation-growth process is taking place during this acceleratory period. For each chromate (V) studied here, the acceleratory period is followed by a period of continuously decreasing rate, to which can be applied, with equal validity, both first order and contracting plate kinetics. The thermal activation energies for the decay stage of the decomposition of the lanthanide chromates (V) studied in the present work, and also for the chromates (V) of lanthanum, neodymium and samarium [Darrie (1967)], are compared, in Table XLIV, with the energies of the first charge transfer band in the spectra of the corresponding chromates (V).

TABLE XLIV

COMPARISON OF THERMAL ACTIVATION AND CHARGE TRANSFER ENERGIES FOR LANTHANIDE CHROMATES (V)

Compound	Activation Energy for Decay Period (cm^{-1})	Energy of $t_1 \rightarrow {}^1e$ Transition (cm^{-1})
$La\ CrO_4$	$25,500 \pm 2,100$	25,600
$Pr\ CrO_4$	$29,300 \pm 7,000$	25,300
$Nd\ CrO_4$	$20,600 \pm 2,100$	24,500
$Sm\ CrO_4$	$22,000 \pm 2,100$	25,000
$Gd\ CrO_4$	$29,700 \pm 3,800$	25,000
$Tb\ CrO_4$	$31,100 \pm 5,200$	25,000
$Dy\ CrO_4$	$29,000 \pm 6,600$	24,700
$Ho\ CrO_4$	$28,600 \pm 4,200$	24,700
$Er\ CrO_4$	$25,150 \pm 5,250$	24,700
$Yb\ CrO_4$	$22,700 \pm 5,900$	24,400
$Y\ CrO_4$	$27,600 \pm 3,800$	25,000

As can be seen from Table XLIV, the thermal activation energy and the energy of the chromate (V) first charge transfer transition agree in many cases within the limits of experimental error, as for the chromates (VI). There are however several reasons why the same mechanism as was applied to the chromates (VI) cannot be considered applicable to the chromates (V):-

(a) The values of thermal activation energy for the decomposition of the chromates (V) of neodymium, samarium, gadolinium and terbium do not agree with the respective charge transfer energies.

(b) The thermal activation energies for the chromates (V) of neodymium and samarium, to the highest limit of experimental error, are lower than the values of the charge transfer energies. Such values cannot be explained on

the basis of transfer of energy between chromate (V) groups.

(c) Structural factors - with the exception of lanthanum chromate (V) which has the monoclinic Huttonite structure [Schwarz (1963)], the chromates (V) studied here all have the tetragonal zircon structure. As can be seen from Table XLIV, there is a significant variation in the values of thermal activation energy found for these chromates (V). If the mechanism suggested for the decomposition of lanthanide chromates (VI), viz. a single electron transfer from co-ordinated oxygen to the central chromium atom as the activation step with transmission of the energy to the surface along the chains of chromate (VI) tetrahedra, was also applicable to the decomposition of lanthanide chromates (V), no significant variation in values of thermal activation energy would be expected: all the compounds having the same crystal structure and hence the same ability to propagate energy.

Values for the oscillator strengths of chromate (V) transitions are not available from the literature, but from analogy with other transition metal oxy-anions e.g. chromate (VI) [Wolfsberg and Helmholtz (1952)]; molybdate (VI) and tungstate (VI) anions [Blasse and Bril (1966)] and vanadate (V) anion [Ropp (1968)] where the oscillator strength is low, this is also likely to be the case with the chromate (V) anion. This would mean that the chromate (V) group could take part in energy transfers only where the short range exchange mechanism is applicable, since a high oscillator strength is necessary for energy transfers involving interaction of dipole fields. The requirements for efficient transfer by an exchange mechanism are

(i) orbital overlap between the transmitting and the receiving group and (ii) energy overlap between the emission band of the transmitting group and the absorption band of the receiving group. No data is available on the emission energies of the chromate (V) group, but it is likely that there is at least a small degree of overlap with the absorption band. From a model of the zircon structure (kindly made to scale by Dr. C.A. Beevers) it is estimated that the closest proximity of oxide ions from neighbouring chromate (V) groups is approximately 2.9 - 3.0 Å, while the sum of ionic radii for two oxide ions is 2.80 Å. It would appear therefore, that the presence of the lanthanide ion between neighbouring chromate (V) groups keeps them sufficiently far apart for there to be little or no orbital overlap between them, and hence makes energy transfer by exchange between them unlikely.

There are two main properties of the lanthanide ion which might be expected to influence the mechanism of decomposition. These are:- (a) The polarising power and (b) the electronic energy levels. If the variation in thermal activation energies was dependent on the ionic radius or on the polarising power of the lanthanide ion having an effect on the separation of neighbouring chromate (V) groups, a fairly regular trend down the lanthanide series would be expected; since this is not the case, it is suggested that the values of thermal activation energy are dependent on the energy levels of the 4f electrons of the lanthanide ions and the following mechanism is proposed and discussed below. (Since neither the La^{3+} nor the Y^{3+} ions has any 4f electrons this mechanism cannot be applied to them and the decomposition of the chromates (V) of these ions are discussed separately at a later stage.)

(a) Activation Step - absorption of thermal energy by the chromate (V) group causing electron transfer from co-ordinated oxygen to the central chromium.

(b) Propagation of energy to surface - (i) Transfer of energy from chromate (V) group to nearest lanthanide ion. (ii) Transfer of energy to the surface along rows of lanthanide ions.

(c) Decomposition at the surface - transfer of energy from a lanthanide ion to a chromate (V) group, which then decomposes.

The stages involved in this mechanism are now considered individually. Step (a) - the activation process - needs no further discussion as this has been covered in the case of the chromates (VI).

Several well established cases of absorption of energy by transition - metal oxy-anions and subsequent transfer to a lanthanide ion are known in the field of inorganic phosphors [Ropp (1968); Blasse and Bril (1966); Blasse (1966); Botden (1951)] and a fairly comprehensive survey of the mechanisms of such transfers has been given by Dexter (1953). Since the oscillator strength of the chromate (V) group is low and oscillator strengths of lanthanide ions are also known to be low [Blasse and Bril (1966)], interaction of dipole fields is not likely and transfer here is likely to be by an exchange mechanism. The two conditions for efficient transfer by exchange are:-

(i) Good orbital overlap between the two centres.

(ii) Energy overlap between the emission band of the transmitting group and the absorption band of the receiving group.

It has been shown [Blasse and Bril (1966)] that where orbital overlap can be attained using an O^{2-} ion as an intermediary, the efficiency of the exchange is dependent on the Ln - O^{2-} - M angle.

If this angle is 180°, the probability of exchange is high, while if the angle is 90°, the probability of exchange is low. Examination of a scale model of the zircon structure shows that in these lanthanide chromates (V), this angle is of the order of 160° and hence exchange should take place.

In these compounds, the energy overlap is dependent on two factors:-

(i) The emission band of the chromate (V) group.

(ii) The energy levels of the lanthanide ions.

No information is available from the literature on the emission band of the chromate (V) group. It seems reasonable to assume however that the emission band will be fairly broad and will lie at a somewhat higher energy than the absorption band, since this is the case with the tungstate ion [Dexter (1953)] where the absorption peaks at 240 nm. and the emission peaks at 420 nm. but there is still a small degree of overlap between them.

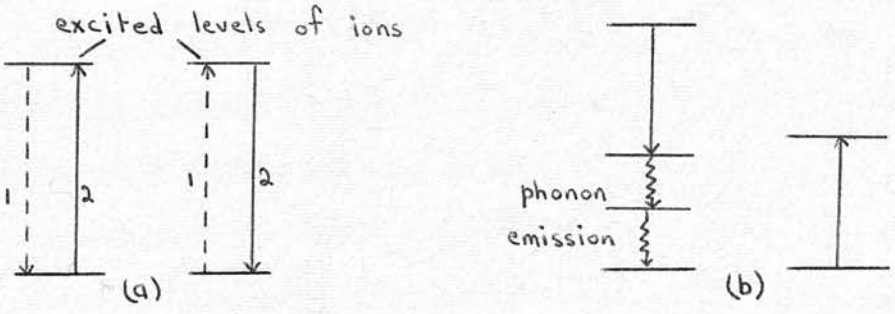
Most of the lanthanide ions have several energy levels between the ground state and 30,000 cm^{-1}, but for many of them, no information is available on the levels above 20,000 cm^{-1}. It is known however, that the first excited state of the Gd^{3+} ion is the $^6P_{7/2}$ state at 32,066 cm^{-1} above the ^8S ground state [Dieke and Hall (1957)] and this then is the minimum energy which would be required if transfer of energy to the Gd^{3+} ion is to occur. This value does in fact lie within the experimental error of the value for thermal activation energy of 29,700 $\pm$ 3,800 cm^{-1}. Further evidence for this proposed mechanism comes from the decomposition of terbium chromate (V). The Tb^{3+} ion has two fairly high energy excited states, $^5D_3$ at approximately 26,000 cm^{-1} and $^5D_4$ at 20,500 cm^{-1}, with the next state below

these lying only 6,000 cm^{-1} above the ground state [Van Uitert and Johnson (1966)]. The energy gap between the $^5D_3$ and $^5D_4$ levels should be sufficiently large for any energy transferred to the $^5D_3$ state to be retained there and not lost to the $^5D_4$ level since only fairly small amounts of electronic energy can be dissipated by interaction with the lattice. This value of 26,000 cm^{-1}, the energy required for transfer into the $^5D_3$ level of the Tb^{3+} ion agrees, within the limits of experimental error, with the value of thermal activation energy (31,000 $\pm$ 5,200 cm^{-1}) found for terbium chromate (V). In the case of erbium chromate (V), the Er^{3+} ion has several levels in the range 22,500 to 28,000 cm^{-1} [Johnson, Van Uitert, Tubin and Thomas (1964)] which might be suitable for accepting the correct amount of transferred energy; and for Pr^{3+}, the $^3P_2$ level lies at approximately 22,000 cm^{-1} above the ground state [Wong and Richman (1962)] and again might be a suitable acceptor level, although there may be other more suitable levels above this for which values are not yet known. For the remaining lanthanide ions, values for the energy states lying greater than 20,000 cm^{-1} above the ground states are not available from the literature.

As was stated previously, for the chromates (V) of neodymium and samarium, the thermal activation energy is found to be lower than the energy of the chromate (V) charge transfer transition. This could not be readily explained on the basis of energy transfer between chromate (V) groups, but might be explicable with the mechanism proposed here if the only available energy level for each of these lanthanide ions lies in the range 20,000 - 24,000 cm^{-1} above the ground state, but still maintains some degree of overlap with the chromate (V) emission band, i.e. absorbs an energy at the low end of the broad

emission band.

The third stage in the proposed mechanism viz. the transfer of the activation energy to the surface of a particle, is now discussed. There is no evidence from the literature of energy, having been transferred from an anion to a lanthanide ion by an exchange mechanism, then being transferred back to an anion. There are however, some known mechanisms of energy transfer between lanthanide ions [Van Uitert and Johnson (1966)]. Due to the relatively large distances between lanthanide ions in the zircon structure (approximately 3.5Å), energy transfer by exchange is unlikely to occur. Dexter (1953) has shown however that multipolar interactions may occur for separations as great as 20 Å. Accordingly, where such interactions are strong, as for the lanthanide ions [Van Uitert and Johnson (1966)], multipolar resonance and multipolar transfer are likely to take place. Multipolar resonance is a reversible energy transfer transition between two ions which have levels at equal energies (See (a) below). Multipolar transfer involves energy transfer from one ion to a lower lying level of a second ion by transitions that are matched in energy and is associated with phonon emission (See (b) below).



(a) Multipolar resonance (reversible)

(b) Multipolar Transfer

Since in these chromates (V), only ions belonging to one member of the lanthanides are present in each compound, neighbouring ions are certain to have exactly matched energy levels and hence transfer by multipolar resonance may occur.

At the surface of a particle, the energy levels of the chromate (V) groups will be different from those of chromate (V) groups at normal lattice sites and may then act as 'energy sinks' [Dexter and Schulman (1954)] by absorbing the energy reaching the surface via the lanthanide ions and thus decomposing.

The two compounds, lanthanum chromate (V) and yttrium chromate (V), in which the lanthanide ion has no 4f electrons, are now discussed. Neither the La^{3+} ion nor the Y^{3+} ion has transitions in the ultraviolet or visible range and therefore no suitable energy levels on which to base a mechanism involving energy transfer from chromate (V) group to lanthanide ion. Lanthanum chromate (V) however also differs from the chromates (V) discussed previously in that the crystal structure is of the Huttonite rather than the zircon type. Lanthanum chromate (V) [Schwarz (1963)] is isomorphous with the monoclinic modification of cerium phosphate in which the oxygens form a tightly packed structure [Mooney (1948)]. Lanthanum chromate (V) will also therefore have a tightly packed lattice of oxide ions with the chromium atoms occupying tetrahedral holes. This may mean that in lanthanum chromate (V), orbital overlap between neighbouring chromate (V) groups is sufficiently good for activation energy to be transferred to the surface by exchange between the chromate (V) groups without involvement of the lanthanide ion.

The case of yttrium chromate (V) is rather more difficult to explain, since, as well as having no correctly positioned energy levels on the Y^{3+} ion, this compound also has the zircon type

structure. On considering the fundamental properties of the yttrium ion, as compared to the lanthanide ions, the major difference between them lies in the electronic configuration, since the ionic radius of the Y^{3+} ion (0.90 Å) is very similar to those of the lanthanides (Dy^{3+} - 0.91 Å; Ho^{3+} - 0.89 Å). In the trivalent lanthanide ions, the outer shell containing the 5s and 5p orbitals is separated from the 4d orbitals by the 4f electrons and hence no mixing of orbitals occurs. In the trivalent yttrium ion however, there are no f electrons present and mixing between the full 3d levels and the 4s and 4p levels will lead to a higher electron density at the surface of the ion than occurs with the lanthanide ions. It is possible therefore that stronger repulsive forces between the outer electrons of the yttrium ions and the outer electrons on the oxide ions may sufficiently distort the electron clouds around the oxide ions for orbital overlap between neighbouring chromate (V) ions to become possible. It should be noted that the distance between oxide ions on neighbouring chromate (V) groups in the zircon structure is normally in the range 2.9 - 3.0 Å while the sum of the normal ionic radii of two oxide ions is 2.8 Å. It would not therefore require a great deal of distortion of the electron clouds to allow overlap between two oxide ions. If this is the case, transfer of energy by an exchange mechanism between neighbouring chromate (V) groups may also be applicable in the decomposition of yttrium chromate (V).

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APPENDIX

TABLE A I

dÅ SPACING FOR PRASEODYMIUM CHROMATE V

Literature				Measured		Calculated	Plane at Reflection
Zirconite		Huttonite				zirconite	
d	Int	d	Int	d	Int	d	
4.87	19			4.87	37	4.84	011
		4.69	17				
		4.33	28				
3.69	78			3.69	100	3.67	020
		3.55	28				
		3.35	69	3.36	26		
		3.16	100	3.16	39		
		3.04	22				
		2.903	69	2.931	43		
2.675	31					2.733	112
2.578	17			2.600	26	2.597	220
2.281	11			2.293	26	2.288	031
		2.238	17				
		2.206	23				
2.049	11					2.057	013
		1.981	28				
1.941	17	1.945	23			1.942	321
		1.918	23				
1.884	17	1.880	33	1.888	57		

Reference - Schwarz (1963)

- Bertaut, Buisson and Mareschal (1964)

TABLE A II

dÅ SPACINGS FOR GADOLINIUM CHROMATE (V)

Measured		Calculated			
d	Int	h	k	l	d
4.69	23	0	1	1	4.746
3.59	100	0	2	0	3.602
		1	2	1	2.869
2.675	63	1	1	2	2.683
2.535	22	2	2	0	2.548
2.333	22	0	2	2	2.373
2.233	20	0	3	1	2.244
2.014	23	0	1	3	2.019
1.899	21	3	2	1	1.905
1.845	67	3	1	2	1.847
1.791	26	0	4	0	1.801

Reference: - Bertaut, Buisson and Mareschal (1964)

TABLE A III

dÅ SPACINGS FOR TERBIUM CHROMATE (V)

Measured		Calculated			
d	Int	h	k	l	d
4.74	27	0	1	1	4.730
3.60	100	0	2	0	3.584
2.903	15	1	2	1	2.856
2.675	78	1	1	2	2.673
2.535	27	2	2	0	2.535
2.362	12	0	2	2	2.365
2.233	20	0	3	1	2.234
2.014	12	0	1	3	2.014
1.891	13	3	2	1	1.896
1.841	58	3	1	2	1.840
1.791	24	0	4	0	1.792

Reference - Bertaut, Buisson and Mareschal (1964)

TABLE A IV

dÅ SPACINGS FOR DYSPROSIUM CHROMATE (V)

Measured		Calculated			
d	Int	h	k	l	d
4.65	40	0	1	1	4.714
3.56	100	0	2	0	3.571
2.823	16	1	2	1	2.847
2.659	75	1	1	2	2.664
2.515	32	2	2	0	2.526
2.344	17	0	2	2	2.357
2.217	27	0	3	1	2.226
2.002	23	0	1	3	2.008
1.863	17	3	2	1	1.889
1.824	68	3	1	2	1.834
1.781	21	0	4	0	1.784

Reference:- Bertaut, Buisson and Mareschal (1964)

TABLE A V

dÅ SPACINGS FOR HOLMIUM CHROMATE (V)

Measured		Calculated			
d	Int	h	k	l	d
4.69	21	0	1	1	4.699
3.55	100	0	2	0	3.562
2.832	10	1	2	1	2.838
2.652	68	1	1	2	2.652
2.515	20	2	2	0	2.518
2.350	8	0	2	2	2.346
2.217	17	0	3	1	2.219
1.998	10	0	1	3	2.001
1.880	10	3	2	1	1.883
1.827	54	3	1	2	1.828
1.778	17	0	4	0	1.780

TABLE A VI

dÅ SPACINGS FOR ERBIUM CHROMATE (V)

Measured		Calculated			
d	Int	h	k	l	d
4.69	25	0	1	1	4.684
3.55	100	0	2	0	3.549
2.823	12	1	2	1	2.828
2.644	65	1	1	2	2.650
2.502	22	2	2	0	2.507
2.344	10	0	2	2	2.343
2.212	18	0	3	1	2.212
1.994	15	0	1	3	1.996
1.870	15	3	2	1	1.877
1.820	56	3	1	2	1.821
1.772	20	0	4	0	1.773

Reference : Bertaut, Buisson and Mareschal (1964)

TABLE A VII

dÅ SPACINGS FOR YTTERBIUM CHROMATE (V)

Measured		Calculated			
d	Int	h	k	l	d
4.67	34	0	1	1	4.665
3.53	100	0	2	0	3.530
2.814	12	1	2	1	2.814
2.637	71	1	1	2	2.638
2.488	26	2	2	0	2.496
2.327	8	0	2	2	2.332
2.196	17	0	3	1	2.200
1.990	14	0	1	3	1.988
1.870	20	3	2	1	1.867
1.810	67	3	1	2	1.813
1.765	21	0	4	0	1.765

Reference : Bertaut, Buisson and Mareschal (1964)

TABLE A VIII

dÅ SPACINGS FOR YTTRIUM CHROMATE (V)

Measured		Calculated			
d	Int	h	k	l	d
4.65	9	0	1	1	4.695
3.53	100	0	2	0	3.557
		1	2	1	2.835
2.644	66	1	1	2	2.657
2.502	28	2	2	0	2.515
2.338	10	0	2	2	2.348
2.212	16	0	3	1	2.217
1.998	11	0	1	3	2.000
1.873	11	3	2	1	1.881
1.820	58	3	1	2	1.826
1.775	24	0	4	0	1.778

Reference:- Bertaut, Buisson and Mareschal (1964)

TABLE A IX

dÅ SPACINGS FOR PRASEODYMIUM CHROMATE (VI)

$Pr_2(CrO_4)_3$.Hydrated			Anhydrous $Pr_2(CrO_4)_3$		
Measured		Literature	Measured		Literature
d	Int	d	d	Int	d
9.12	100		6.51	85	
5.28	36	N	5.37	77	N
4.74	19	O	3.62	73	O
4.58	22	N	3.53	72	N
4.25	20	E	3.05	100	E
1.88	23		2.86	75	
			2.49	48	

TABLE A X

dÅ SPACINGS FOR $PrCrO_3$

Measured		Calculated			
d	Int	h	k	l	d
		0	1	1	4.467
		1	1	0	3.863
3.85	18	0	0	2	3.859
		1	1	1	3.454
		0	1	2	3.155
		0	2	0	2.739
		1	1	2	2.730
2.722	100	2	0	0	2.724
2.571	7	0	2	1	2.581
		1	2	1	2.333
2.327	8	2	1	1	2.326
2.222	22	2	0	2	2.226
2.141	10	1	1	3	2.141
		1	2	2	2.068
		2	1	2	2.061
		2	2	0	1.933
1.929	37	0	0	4	1.928
		0	2	3	1.876
1.873	12	2	2	1	1.875

Reference : Schneider, Roth and Waring (1961)

TABLE A XI

dÅ SPACINGS FOR $GdCrO_3$

Measured		Calculated			
d	Int	h	k	l	d
		0	1	1	4.466
3.82	21	1	1	0	3.826
		0	0	2	3.805
3.40	26	1	1	1	3.418
3.10	39	0	1	2	3.132
2.746	22	0	2	0	2.757
2.698	100	1	1	2	2.698
2.652	44	2	0	0	2.656
2.593	27	0	2	1	2.592
		1	2	1	2.330
		2	1	1	2.283
2.161	20	1	1	3	2.115
		1	1	3	2.115
		1	2	2	2.058
		2	1	2	2.025
1.907	56	2	2	0	1.914
1.891	36	0	0	4	1.904
1.831	24	2	2	1	1.856
1.803	24	0	1	4	1.798

Reference:- Schneider, Roth and Waring (1961)

:- S. Quezel-Ambrunaz and M. Mareschal (1963)

TABLE A XII

dÅ SPACINGS FOR $TbCrO_3$

Measured		Calculated			
d	Int	h	k	l	d
		0	1	1	4.513
3.80	24	1	1	0	3.851
		0	0	2	3.788
3.39	15	1	1	1	3.430
3.07	45	0	1	2	3.141
		0	2	0	2.809
2.746	27	1	1	2	2.701
2.675	100	2	0	0	2.646
2.637	36	0	2	1	2.634
2.368	18	1	2	1	2.358
2.217	17	2	1	1	2.282
2.166	23	2	0	2	2.167
		1	1	3	2.113
2.098	15	1	2	2	2.076
		2	2	0	1.926
1.907	26	0	0	4	1.894
1.888	36	0	2	3	1.878
1.855	24	2	2	1	1.866
1.814	15	0	1	4	1.794

Reference : Schneider, Roth and Waring (1961)

: Quesel-Ambrunaz and Mareschal (1963)

TABLE A XIII

dÅ SPACINGS FOR $DyCrO_3$

Measured		Calculated			
d	Int	h	k	l	d
		0	1	1	4.44
		1	1	0	4.31
3.75	21	0	2	0	3.751
3.39	25	1	1	1	3.393
3.06	61	0	2	1	3.100
2.730	25	0	0	2	2.755
2.667	100	1	2	1	2.671
2.621	38	2	0	0	2.630
2.578	19	0	1	2	2.586
		1	1	2	2.321
2.260	20	2	1	1	2.263
2.156	22	2	2	0	2.154
2.041	23	1	2	2	2.045
		2	2	1	2.005
1.899	26	2	0	2	1.903
1.841	32	2	1	2	1.844

Reference:- Schneider, Roth and Waring (1961)

:- Quezel-Ambrunaz and Mareschal (1963)

TABLE A XIV

dA SPACINGS FOR $HoCrO_3$

Measured		Calculated			
d	Int	h	k	l	d
4.33	18	0	1	1	4.45
3.78	25	1	1	0	3.801
		0	0	2	3.768
3.36	21	1	1	1	3.394
3.05	63	0	1	2	3.112
2.754	31	0	2	0	2.759
2.667	100	1	1	2	2.677
2.614	31	2	0	0	2.621
		0	2	1	2.592
		1	2	1	2.307
		2	1	1	2.259
2.122	17	2	0	2	2.151
2.076	18	1	1	3	2.095
2.045	13	1	2	2	2.050
		2	1	2	2.005
1.899	27	2	2	0	1.900
1.873	35	0	0	4	1.884
		0	2	3	1.858
1.834	21	2	2	1	1.842

Reference : Schneider, Roth and Waring (1961)

: Quezel-Ambrunaz and Mareschal (1963)

TABLE A XV

dÅ SPACINGS FOR $ErCrO_3$

Measured		Calculated			
d	Int	h	k	l	d
		0	1	1	4.443
4.29	14	1	1	0	4.286
3.78	22	0	2	0	3.755
3.39	21	1	1	1	3.384
3.04	100	0	2	1	3.103
2.754	15	0	0	2	2.755
2.667	80	1	2	1	2.667
2.614	24	2	0	0	2.610
2.593	15	0	1	2	2.587
		1	1	2	2.317
2.260	10	2	1	1	2.251
2.146	12	2	2	0	2.143
2.066	13	1	2	2	2.044
1.994	14	2	2	1	1.996
1.895	19	2	0	2	1.895
1.884	17	0	4	0	1.877
1.863	44	0	3	2	1.853
1.838	13	2	1	2	1.837
1.814	9	2	3	0	1.809

Reference:- Schneider, Roth and Waring (1961)

:-Quezel-Ambrunaz and Mareschal (1963)

TABLE A XVI

dA SPACINGS FOR $YbCrO_3$

Measured		Calculated			
d	Int	h	k	l	d
4.25	10	0	1	1	4.438
3.77	28	1	1	0	3.781
		0	0	2	3.745
3.37	24	1	1	1	3.375
3.01	84	0	1	2	3.097
2.754	22	0	2	0	2.755
2.659	100	1	1	2	2.660
2.614	55	2	0	0	2.597
		0	2	1	2.586
		1	2	1	2.315
2.217	18	2	1	1	2.242
2.136	14	2	0	2	2.135
2.071	12	1	1	3	2.084
2.049	12	1	2	2	2.040
		2	1	2	1.991
1.888	23	2	2	0	1.891
1.870	24	0	0	4	1.872
1.845	50	0	2	3	1.850

Reference : Schneider, Roth and Waring (1961)

: Quezel-Ambrunaz and Mareschal (1963)

TABLE A XVII

dÅ SPACINGS FOR $YCrO_3$

Measured		Calculated			
d	Int	h	k	l	d
		0	1	1	4.457
		1	1	0	3.803
3.74	14	0	0	2	3.780
3.37	18	1	1	1	3.397
3.06	17	0	1	2	3.118
2.754	23	0	2	0	2.759
2.675	100	1	1	2	2.681
2.621	27	2	0	0	2.624
2.585	11	0	2	1	2.592
		1	2	1	2.324
		2	1	1	2.261
2.146	16	2	0	2	2.157
2.094	16	1	1	3	2.101
		1	2	2	2.051
		2	1	2	2.008
1.903	30	2	2	0	1.902
1.880	27	0	0	4	1.890
		0	2	3	1.860
1.845	17	2	2	1	1.844

Reference:- Schneider, Roth and Waring (1961)

TABLE A XVIII

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS PRASEODYMIUM CHROMATE (VI) AT 594°C

Time t (mins.)	$t^{1.74}$	Fraction Decomposed (x)
0	0	0
10	0	0
20	183.5	0.0047
30	371.5	0.0142
40	613.1	0.0191
50	904.2	0.0319
60		0.0412
70		0.0603
80		0.0731
90		0.0938
100		0.1129
110		0.1303
120		0.1478
130		0.1652
140		0.1922
150		0.2113
160		0.2399
170		0.2653
180		0.2876
190		0.3193
200		0.3479
210		0.3686
220		0.4003
230		0.4289
240		0.4496

TABLE A XIX

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS

PRASEODYMIUM CHROMATE(VI) AT 599°C

Time t (mins)	$t^{1.7}$	Fraction Decomposed (x)
0	0	0
10	50.1	0.0032
20	162.9	0.0142
30	324.3	0.0286
40	528.9	0.0508
50	773.2	0.0731
60	1053.0	0.1048
70		0.1318
80		0.1699
90		0.2079
100		0.2381
110		0.2794
120		0.3206
130		0.3650
140		0.4111
150		0.4588
160		0.5000
170		0.5429
180		0.5857
190		0.6269
200		0.6667
210		0.7016
220		0.7333
230		0.7636
240		0.7952

TABLE A XX

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS PRASEODYMIUM CHROMATE (VI) AT 600°C

Time t (mins)	$t^{1.55}$	Fraction Decomposed (x)
0	0	0
10	35.5	0.0095
20	103.9	0.0319
30	194.7	0.0589
40	304.2	0.0891
50	430.0	0.1305
60	570.1	0.1735
70	724.1	0.2261
80		0.2768
90		0.3247
100		0.3757
110		0.4266
120		0.4775
130		0.5315
140		0.5825
150		0.6334
160		0.6811
170		0.7290
180		0.7718
190		0.8053
200		0.8388
210		0.8721
220		0.8993
230		0.9200
240		0.9391

TABLE A XXI

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS

PRASEODYMIUM CHROMATE(VI) AT 603°C

Time t (mins)	$t^{1.56}$	Fraction Decomposed (x)
0	0	0
10	36.3	0.0128
20	107.0	0.0349
30	201.4	0.0731
40	315.6	0.1208
50	447.1	0.1766
60	593.9	0.2353
70	755.4	0.2925
80		0.3497
90		0.4135
100		0.4770
110		0.5375
120		0.5994
130		0.6536
140		0.7124
150		0.7601
160		0.8014
170		0.8395
180		0.8730
190		0.8984
200		0.9239
210		0.9398
220		0.9621
230		0.9731
240		0.9907

TABLE A XXII

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS PRASEODYMIUM CHROMATE (VI) AT 606°C

Time t (mins)	$t^{1.64}$	Fraction Decomposed (x)
0	0	0
10	43.65	0.0158
20	136.0	0.0540
30	264.4	0.1096
40	424.0	0.1715
50	611.5	0.2335
60	824.5	0.3019
70		0.3733
80		0.4496
90		0.5243
100		0.5942
110		0.6640
120		0.7180
130		0.7736
140		0.8230
150		0.8674
160		0.9040
m170		0.9342
180		0.9549
190		0.9818
200		0.9977
210		1.0089

TABLE A XXIII

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS

PRASEODYMIUM CHROMATE(VI) AT 615°C

Time t (mins)	$t^{1.40}$	Fraction Decomposed (x)
0	0	0
10	25.1	0.0666
20	66.3	0.1746
30	116.9	0.2921
40	174.9	0.4223
50	241.8	0.5555
60	308.4	0.6698
70	382.8	0.7666
80		0.8509
90		0.9175
100		0.9682
110		1.0064

TABLE A XXIV

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS

PRASEODYMIUM CHROMATE(VI) AT 617°C

Time t (mins)	$t^{1.32}$	Fraction Decomposed (x)
0	0	0
10	20.9	0.0968
20	52.2	0.2365
30	89.0	0.3937
40	130.2	0.5476
50		0.6858
60		0.7999
70		0.8937
80		0.9603
90		1.0190

TABLE A XXV

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS

PRASEODYMIUM CHROMATE(VI) AT 618°C

Time t (mins)	$t^{1.29}$	Fraction Decomposed (x)
0	0	0
10	19.5	0.1130
20	47.9	0.2642
30	80.4	0.4201
40	116.6	0.5809
50		0.7178
60		0.8388
70		0.9247
80		0.9868

TABLE A XXVI

FIRST STAGE OF DECOMPOSITION OF ANHYDROUS PRASEODYMIUM CHROMATE (VI) AT 627°C

Time t (mins)	$t^{1.21}$	Fraction Decomposed (x)
0	0	0
10	16.2	0.1575
20	37.5	0.3674
30	61.3	0.5836
40	86.8	0.7601
50		0.8968
60		0.9970

TABLE A XXVII

FIRST STAGE OF DECOMPOSITION OF ANHYROUS

PRASEODYMIUM CHROMATE (VI) AT 628°C

Time t(mins)	$t^{1 \cdot 13}$	Fraction Decomposed (x)
0	0	0
10		0.2159
20	29.5	0.4829
30	46.7	0.7290
40	64.6	0.9184
50		1.0301

TABLE A XXVIII

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 616°C

Time t (mins)	$t^{1\cdot29} \times 10^{-2}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0		0		
10		0.0064		
20		0.0193		
30		0.0322		
40		0.0467		
50		0.0612	0.0274	0.0311
60	1.928	0.0741	0.0334	0.0378
70	2.350	0.0918	0.0418	0.0470
80	2.789	0.1095	0.0513	0.0563
90	3.244	0.1256	0.0584	0.0649
100	3.715	0.1449	0.0679	0.0753
110	4.200	0.1659	0.0789	0.0867
120	4.697	0.1836	0.0881	0.0965
130	5.205	0.2045	0.0993	0.1081
140	5.724	0.2254	0.1109	0.1199
150	6.256	0.2464	0.1229	0.1319
160		0.2641	0.1332	0.1422
170		0.2882	0.1476	0.1563
180		0.3043	0.1574	0.1659
190		0.3253	0.1709	0.1786
200		0.3430	0.1824	0.1894
210		0.3704	0.2009	0.2065
220		0.3849	0.2111	0.2157
230		0.4026	0.2235	0.2271
240		0.4219	0.2380	0.2397

TABLE A XXIX

DECOMPOSITION OF PRASEODYMIUM CHROMATE (V) AT 622°C

Time t (mins)	$t^{1.36} \times 10^{-2}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0194		
20		0.0355		
30		0.0484		
40		0.0661		
50		0.0806		
60	2.653	0.0952	0.0433	0.0627
70	3.273	0.1177	0.0544	0.0765
80	3.925	0.1419	0.0664	0.0925
90	4.609	0.1661	0.0789	0.1087
100	5.321	0.1919	0.0923	0.1260
110	6.059	0.2194	0.1075	0.1438
120	6.822	0.2468	0.1232	0.1610
130		0.2726	0.1383	0.1776
140		0.2968	0.1529	0.1925
150		0.3194	0.1671	0.2097
160		0.3484	0.1861	0.2252
170		0.3677	0.1993	0.2432
180		0.3952	0.2183	0.2616
190		0.4194	0.2360	0.2759
200		0.4387	0.2509	0.2894
210		0.4694	0.2754	0.3044
220		0.4855	0.2887	0.3233
230		0.5048	0.3051	0.3341
240		0.5258	0.3240	0.3502

TABLE A XXX

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 626°C

Time t (mins)	$t^{1\cdot32} \times 10^{-2}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0178		
20		0.0275		
30		0.0534		
40		0.0728		
50		0.0987		
60	2.179	0.1214	0.0561	
70	2.669	0.1472	0.0693	0.0765
80	3.181	0.1764	0.0842	0.0925
90	3.714	0.2055	0.1000	0.1087
100	4.266	0.2362	0.1168	0.1260
110	4.835	0.2670	0.1348	0.1438
120		0.2961	0.1526	0.1610
130		0.3236	0.1697	0.1776
140		0.3479	0.1858	0.1925
150		0.3754	0.2044	0.2097
160		0.3997	0.2217	0.2252
170		0.4272	0.2420	0.2432
180		0.4547	0.2634	0.2616
190		0.4757	0.2804	0.2759
200		0.4951	0.2969	0.2894
210		0.5162		
220		0.5421		
230		0.5566		
240		0.5777		

TABLE A XXXI

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 628°C

Time t (mins)	$t^{1.34} \times 10^{-2}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0162		
20		0.0653		
30		0.1240		
40	1.381	0.1794	0.0457	
50	1.862	0.2316	0.0633	0.0704
60	2.375	0.2953	0.0823	0.0907
70	2.918	0.3556	0.1035	0.1123
80	3.487	0.4111	0.1235	0.1326
90		0.4649	0.1495	0.1582
100		0.5122	0.1730	0.1805
110		0.5563	0.2022	0.2077
120		0.6003	0.2264	0.2294
130		0.6378	0.2596	0.2582
140		0.6721	0.2804	
150		0.6966		
160		0.7308		
170		0.7586		
180		0.7749		
190		0.7993		
200		0.8157		
210		0.8320		
220		0.8483		
230		0.8613		
240		0.8744		

TABLE A XXXII

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 630°C

Time t (mins)	$t^{1\cdot30} \times 10^{-2}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0178		
20		0.0421		
30	0.820	0.0761		
40	1.192	0.1133		
50	1.592	0.1521		
60	2.016	0.1926	0.0930	0.1014
70	2.461	0.2314	0.1142	0.1233
80		0.2686	0.1358	0.1448
90		0.3107	0.1617	0.1698
100		0.3528	0.1889	0.1955
110		0.3883	0.2135	0.2179
120		0.4239	0.2395	0.2410
130		0.4595	0.2672	0.2648
140		0.4968	0.2983	0.2906
150		0.5275		
160		0.5599		
170		0.5809		
180		0.6117		
190		0.6375		
200		0.6602		
210		0.6861		
220		0.7055		
230		0.7249		
240		0.7427		

TABLE A XXXIII

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 637°C

Time t (mins)	$t^{1.36} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0.95		
20		0.0537		
30	1.014	0.0961		
40	1.498	0.1433	0.0671	
50	2.028	0.1938	0.0934	0.1021
60	2.599	0.2459	0.1225	0.1316
70		0.2964	0.1526	0.1612
80		0.3485	0.1861	0.1928
90		0.3941	0.2175	0.2216
100		0.4365	0.2492	0.2493
110		0.4821	0.2858	0.2803
120		0.5212		0.3080
130		0.5619		0.3381
140		0.5993		
150		0.6287		
160		0.6645		
170		0.6889		
180		0.7134		
190		0.7459		
200		0.7622		
210		0.7834		
220		0.7980		
230		0.8160		
240		0.8306		

TABLE A XXXIV

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 640°C

me t (mins)	$t^{1.32} \times 10^{-2}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0261		
20		0.0653		
30	0.888	0.1240		
40	1.298	0.1794	0.0859	0.0941
50	1.742	0.2316	0.1142	0.1234
60		0.2953	0.1519	0.1605
70		0.3556	0.1909	0.1973
80		0.4111	0.2300	0.2326
90		0.4649	0.2716	0.2685
100		0.5122	0.3118	0.3016
110		0.5563	0.3530	0.3339
120		0.6003		
130		0.6378		
140		0.6721		
150		0.6966		
160		0.7308		
170		0.7586		
180		0.7749		
190		0.7993		
200		0.8157		
210		0.8320		
220		0.8483		
230		0.8613		
240		0.8744		

TABLE A XXXV

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 641°C

me t (mins)	$t^{1.16} \times 10^{-2}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10	0.145	0.0490		
20	0.323	0.1144	0.0426	0.0589
30	0.516	0.2026	0.0983	0.1070
40	0.722	0.2859	0.1461	0.1550
50		0.3693	0.2004	0.2058
60		0.4444	0.2553	0.2546
70		0.5147		0.3034
80		0.5817		0.3532
90		0.6373		
100		0.6928		
110		0.7353		
120		0.7778		
130		0.8023		
140		0.8333		
150		0.8562		
160		0.8791		
170		0.8922		
180		0.9085		
190		0.9167		
200		0.9248		
210		0.9428		
220		0.9461		
230		0.9477		
240		0.9510		

TABLE A XXXVI

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 647°C

Time t (mins)	$t^{1.35} \times 10^{-2}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0	
10	0.224	0.0606	0.0274	
20	0.572	0.1541	0.0727	0.0803
30	0.990	0.2656	0.1341	0.1430
40		0.3705	0.2012	0.2066
50		0.4623	0.2695	0.2667
60		0.5459		0.3261
70		0.6131		
80		0.6770		
90		0.7295		
100		0.7689		
110		0.8082		
120		0.8344		
130		0.8557		
140		0.8787		
150		0.8934		
160		0.9016		
170		0.9115		
180		0.9262		
190		0.9279		
200		0.9328		
210		0.9410		
220		0.9426		
230		0.9443		
240		0.9459		

TABLE A XXXVII

DECOMPOSITION OF PRASEODYMIUM CHROMATE(V) AT 650°C

Time t (mins)	$t^{1.29} \times 10^{-2}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0	
10	0.193	0.0655	0.0294	
20	0.470	0.1653	0.0788	0.0864
30	0.791	0.2668	0.1348	0.1437
40		0.3715	0.2017	0.2072
50		0.4648	0.2714	0.2684
60		0.5516		
70		0.6219		
80		0.6825		
90		0.7365		
100		0.7791		
110		0.8036		
120		0.8363		
130		0.8625		
140		0.8805		
150		0.8920		
160		0.9083		
170		0.9133		
180		0.9214		
190		0.9280		
200		0.9296		
210		0.9329		
220		0.9411		
230		0.9411		
240		0.9460		

TABLE-A XXXVIII

DECOMPOSITION OF GADOLINIUM CHROMATE(V) AT 700°C

Time t(mins)	Fraction Decomposed (x)	$Log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0		
10	0.0172		
20	0.0823	0.0374	0.0419
30	0.2007	0.0972	0.1061
40	0.3087	0.1605	0.1684
50	0.4065	0.2266	0.2295
60	0.4803	0.2842	0.2791
70	0.5455	0.3424	
80	0.5901		
90	0.6295		
100	0.6518		
110	0.6758		
120	0.6947		
130	0.7153		
140	0.7307		
150	0.7427		
160	0.7599		
170	0.7684		
180	0.7753		
190	0.7839		
200	0.7873		
210	0.7993		
220	0.8045		
230	0.8148		
240	0.8182		

TABLE A XXXIX

DECOMPOSITION OF GADOLINIUM CHROMATE(V) AT 706°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.0244	0.0107	0.0174
20	0.1344	0.0626	0.0695
30	0.2870	0.1470	0.1555
40	0.4070	0.2269	0.2298
50	0.4939	0.2958	0.2883
60	0.5565	0.3532	
70	0.6122		
80	0.6487		
90	0.6713		
100	0.6991		
110	0.7165		
120	0.7270		
130	0.7391		
140	0.7548		
150	0.7652		
160	0.7861		
170	0.7896		
180	0.7930		
190	0.8000		
200	0.8070		
210	0.8104		
220	0.8174		
230	0.8243		
240	0.8278		

TABLE A XL

DECOMPOSITION OF GADOLINIUM CHROMATE(V) AT 711°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0	0	0	0
10	0.0382	0.0170	0.0191
20	0.1910	0.0920	0.1007
30	0.3437	0.1829	0.1900
40	0.4497	0.2593	0.2582
50	0.5295	0.3273	
60	0.5781		
70	0.6250		
80	0.6632		
90	0.6858		
100	0.7083		
110	0.7292		
120	0.7413		
130	0.7535		
140	0.7674		
150	0.7760		
160	0.7969		
170	0.8003		
180	0.8073		
190	0.8125		
200	0.8194		
210	0.8247		
220	0.8333		
230	0.8351		
240	0.8385		

TABLE A XLI

DECOMPOSITON OF GADOLINIUM CHROMATE (V) AT 716°C

Time t (mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.1157	0.0535	0.0596
20	0.3523	0.1886	0.1952
30	0.4940	0.2958	0.2886
40	0.5820		
50	0.6442		
60	0.6857		
70	0.7098		
80	0.7375		
90	0.7530		
100	0.7737		
110	0.7893		
120	0.8031		
130	0.8100		
140	0.8204		
150	0.8290		
160	0.8377		
170	0.8394		
180	0.8446		
190	0.8566		
200	0.8584		
210	0.8601		
220	0.8636		
230	0.8722		
240	0.8756		

TABLE A XLII

DECOMPOSITION OF GADOLINIUM CHROMATE(V) AT 720°C

Time t (mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.1369	0.0641	0.0710
20	0.3778	0.2059	0.2114
30	0.5286	0.3265	0.3134
40	0.6135		
50	0.6655		
60	0.7036		
70	0.7244		
80	0.7470		
90	0.7643		
100	0.7730		
110	0.7868		
120	0.7938		
130	0.8042		
140	0.8128		
150	0.8232		
160	0.8336		
170	0.8388		
180	0.8388		
190	0.8406		
200	0.8440		
210	0.8440		
220	0.8544		
230	0.8544		
240	0.8562		

TABLE A XLIII

DECOMPOSITION OF GADOLINIUM CHROMATE(V) AT 723°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.2387	0.1186	0.1274
20	0.4686	0.2747	0.2710
30	0.5923		
40	0.6620		
50	0.7091		
60	0.7404		
70	0.7666		
80	0.7840		
90	0.7979		
100	0.8118		
110	0.8240		
120	0.8293		
130	0.8467		
140	0.8502		
150	0.8606		
160	0.8659		
170	0.8676		
180	0.8711		
190	0.8763		
200	0.8815		
210	0.8850		
220	0.8850		
230	0.8850		
240	0.8850		

TABLE A XLIV

DECOMPOSITION OF GADOLINIUM CHROMATE(V) AT 727°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10}\frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0	0	0	0
10	0.2830	0.1446	0.1640
20	0.5208	0.3196	0.3079
30	0.6302		
40	0.6910		
50	0.7274		
60	0.7500		
70	0.7743		
80	0.7917		
90	0.8038		
100	0.8194		
110	0.8316		
120	0.8351		
130	0.8403		
140	0.8490		
150	0.8576		
160	0.8628		
170	0.8663		
180	0.8681		
190	0.8681		
200	0.8698		
210	0.8733		
220	0.8767		
230	0.8802		
240	0.8819		

TABLE A XLV

DECOMPOSITION OF GADOLINIUM CHROMATE(V) AT 730°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10}\frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.3606	0.1942	0.2003
20	0.5749	0.3715	0.3481
30	0.6655		
40	0.7230		
50	0.7543		
60	0.7770		
70	0.7979		
80	0.8153		
90	0.8258		
100	0.8397		
110	0.8449		
120	0.8571		
130	0.8693		
140	0.8693		
150	0.8693		
160	0.8746		
170	0.8763		
180	0.8780		
190	0.8833		
200	0.8902		
210	0.8920		
220	0.8972		
230	0.8972		
240	0.8990		

TABLE A XLVI

DECOMPOSITION OF TERBIUM CHROMATE(V) AT 641°C

Time t(mins)	$t^{3\cdot13} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0035		
20		0.0035		
30		0.0052		
40		0.0069		
50	2.079	0.0086		
60	3.680	0.0155		
70	5.960	0.0259		
80	9.051	0.0380		
90	13.080	0.0518		
100	18.20	0.0812		
110	24.52	0.1036		
120	32.21	0.1330		0.0689
130	41.35	0.1658	0.0789	0.0867
140		0.2003	0.0969	0.1059
150		0.2332	0.1152	0.1244
160		0.2694	0.1364	0.1453
170		0.3074	0.1596	0.1678
180		0.3420	0.1818	0.1888
190		0.3713	0.2017	0.2071
200		0.4041	0.2248	0.2280
210		0.4283	0.2427	0.2440
220		0.4542	0.2630	0.2613
230		0.4801	0.2840	
240		0.4974	0.2989	

TABLE A XLVII

DECOMPOSITION OF TERBIUM CHROMATE (V) AT 647°C

Time t(mins)	$t^{3.29} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$\overline{\overline{1-(1-x)^{\frac{1}{2}}}}$
0		0		
10		0		
20		0.0052		
30		0.0087		
40		0.0087		
50	3.888	0.0122		
60	7.084	0.0244		
70	11.76	0.0384		
80	18.25	0.0576		
90	26.87	0.0803		
100	38.02	0.1169		
110		0.1518	0.0716	0.0792
120		0.1972	0.0955	0.1040
130		0.2339	0.1155	0.1248
140		0.2757	0.1402	0.1491
150		0.3194	0.1671	0.1751
160		0.3647	0.1970	0.2029
170		0.3997	0.2217	0.2251
180		0.4328	0.2462	0.2468
190		0.4695	0.2754	0.2717
200		0.4974	0.2989	0.2911
210		0.5166	0.3158	
220		0.5428		
230		0.5637		
240		0.5846		

TABLE A XLVIII

DECOMPOSITION OF TERBIUM CHROMATE (V) AT 650°C

Time t(mins)	$t^{2.80} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0052		
20		0.0086		
30	0.137	0.0086		
40	0.306	0.0225		
50	0.572	0.0397		
60	0.953	0.0587		
70	1.467	0.0950		
80	2.131	0.1382	0.0645	0.0717
90		0.1865	0.0895	0.0980
100		0.2383	0.1183	0.1272
110		0.2936	0.1510	0.1595
120		0.3420	0.1818	0.1888
130		0.3903	0.2148	0.2193
140		0.4335	0.2467	0.2474
150		0.4646	0.2714	
160		0.4957	0.2974	
170		0.5216		
180		0.5440		
190		0.5648		
200		0.5838		
210		0.5907		
220		0.6045		
230		0.6200		
240		0.6269		

TABLE A XLIX

DECOMPOSITION OF TERBIUM CHROMATE (V) AT 656°C

Time t(mins)	$t^{3.21} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0		
20		0.0017		
30	0.561	0.0121		
40	1.416	0.0295		
50	2.899	0.0624		
60	5.211	0.1092		0.0561
70	8.551	0.1716	0.0816	0.0899
80		0.2374	0.1176	0.1266
90		0.2929	0.1504	0.1591
100		0.3570	0.1818	0.1981
110		0.4194	0.2360	0.2381
120		0.4610	0.2684	0.2659
130		0.4991	0.3002	
140		0.5338		
150		0.5511		
160		0.5702		
170		0.5945		
180		0.6031		
190		0.6256		
200		0.6395		
210		0.6499		
220		0.6586		
230		0.6724		
240		0.6863		

TABLE A L

DECOMPOSITION OF TERBIUM CHROMATE(V) AT 658°C

Time t(mins)	$t^{2.87} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0052		
20	0.054	0.0156		
30	0.174	0.0450		
40	0.396	0.1125	0.0518	0.0581
50		0.2059	0.1000	0.1090
60		0.2976	0.1535	0.1621
70		0.3841	0.2106	0.2153
80		0.4464	0.2567	0.2560
90		0.5000	0.3010	
100		0.5450		
110		0.5744		
120		0.6021		
130		0.6176		
140		0.6436		
150		0.6540		
160		0.6678		
170		0.6851		
180		0.6972		
190		0.7024		
200		0.7128		
210		0.7284		
220		0.7353		
230		0.7388		
240		0.7457		

TABLE A LI

DECOMPOSITION OF TERBIUM CHROMATE(V) AT 667°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0		
10	0		
20	0.0156		
30	0.0833	0.0378	0.0426
40	0.1875	0.0902	0.0986
50	0.3021	0.1562	0.1646
60	0.3958	0.2188	0.2229
70	0.4705	0.2763	0.2724
80	0.5295	0.3273	
90	0.5694		
100	0.5938		
110	0.6215		
120	0.6441		
130	0.6684		
140	0.6788		
150	0.6875		
160	0.6944		
170	0.7066		
180	0.7222		
190	0.7292		
200	0.7361		
210	0.7413		
220	0.7431		
230	0.7552		
240	0.7604		

TABLE A LII

DECOMPOSITION OF TERBIUM CHROMATE(V) AT 673°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.0277	0.0119	0.0140
20	0.1696	0.0806	0.0889
30	0.3547	0.1903	0.1966
40	0.4792	0.2833	0.2784
50	0.5519		
60	0.5969		
70	0.6332		
80	0.6644		
90	0.6886		
100	0.7059		
110	0.7215		
120	0.7405		
130	0.7526		
140	0.7595		
150	0.7716		
160	0.7803		
170	0.7872		
180	0.7941		
190	0.7993		
200	0.7993		
210	0.8062		
220	0.8080		
230	0.8149		
240	0.8201		

TABLE A LIII

DECOMPOSITION OF TERBIUM CHROMATE(V) AT 682°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.1076	0.0496	0.0552
20	0.3958	0.2188	0.2229
30	0.5538	0.3504	0.3321
40	0.6233		
50	0.6719		
60	0.7153		
70	0.7396		
80	0.7569		
90	0.7691		
100	0.7865		
110	0.7986		
120	0.8073		
130	0.8212		
140	0.8299		
150	0.8385		
160	0.8455		
170	0.8472		
180	0.8524		
190	0.8559		
200	0.8646		
210	0.8750		
220	0.8785		
230	0.8785		
240	0.8889		

TABLE A LIV

DECOMPOSITION OF DYSPROSIUM CHROMATE(V) AT 635°C

Time t(mins)	$t^{2\cdot40} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0035		
20		0.0088		
30		0.0123		
40		0.0158		
50		0.0158		
60		0.0176		
70		0.0246		
80	0.369	0.0370		
90	0.490	0.0440		
100	0.631	0.0546		
110	0.793	0.0704		
120	0.977	0.0880		
130	1.184	0.1056		
140	1.415	0.1250		
150	1.669	0.1514	0.0712	0.0788
160	1.949	0.1761	0.0842	0.0923
170	2.254	0.2042	0.0993	0.1079
180	2.586	0.2359	0.1168	0.1259
190	2.945	0.2676	0.1351	0.1442
200		0.2958	0.1523	0.1608
210		0.3292	0.1735	0.1810
220		0.3486	0.1861	0.1929
230		0.3785	0.2065	0.2116
240		0.4049	0.2253	0.2286

TABLE A LV

DECOMPOSITION OF DYSPROSIUM CHROMATE(V) AT 638°C

Time t(mins)	$t^{2.77} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0		
20		0		
30		0.0018		
40		0.0018		
50		0.0088		
60		0.0263		
70		0.0368		
80	1.869	0.0561		
90	2.589	0.0860		
100	3.467	0.1158		0.0597
110	4.515	0.1456	0.0682	0.0757
120	5.746	0.1807	0.0867	0.0948
130		0.2211	0.1086	0.1174
140		0.2614	0.1316	0.1406
150		0.2982	0.1538	0.1623
160		0.3263	0.1715	0.1792
170		0.3632	0.1959	0.2020
180		0.3877	0.2130	0.2175
190		0.4105	0.2295	0.2322
200		0.4404	0.2521	
210		0.4579	0.2660	
220		0.4825	0.2860	
230		0.5000		
240		0.5246		

TABLE A LVI

DECOMPOSITION OF DYSPROSIUM CHROMATE (V) AT 641°C

Time t(mins)	$t^{2.77} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0		0		
10		0		
20		0.0035		
30		0.0088		
40		0.0140		
50	0.508	0.0228		
60	0.843	0.0386		
70	1.291	0.0579		
80	1.869	0.0877		
90	2.589	0.1211		0.0625
100		0.1544	0.0730	0.0804
110		0.1965	0.0951	0.1036
120		0.2351	0.1162	0.1254
130		0.2789	0.1422	0.1508
140		0.3193	0.1671	0.1750
150		0.3474	0.1853	0.1922
160		0.3807	0.2081	0.2130
170		0.4070	0.2269	0.2299
180		0.4474	0.2577	0.2566
190		0.4719	0.2774	
200		0.5000	0.3010	
210		0.5228	0.3214	
220		0.5439		
230		0.5596		
240		0.5702		

TABLE A LVII

DECOMPOSITION OF DYSPROSIUM CHROMATE (V) AT 644°C

Time t(mins)	$t^{3.22} \times 10^{-6}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0		
20		0		
30		0		
40		0.0070		
50		0.0105		
60		0.0298		
70	1.336	0.0526		
80	2.081	0.0895		0.0458
90	3.075	0.1281	0.0595	0.0662
100	4.365	0.1754	0.0838	0.0919
110		0.2228	0.1096	0.1184
120		0.2632	0.1326	0.1416
130		0.3088	0.1605	0.1686
140		0.3491	0.1864	0.1932
150		0.3842	0.2106	0.2153
160		0.4140	0.2319	0.2345
170		0.4509	0.2603	
180		0.4719		
190		0.5000		
200		0.5158		
210		0.5404		
220		0.5509		
230		0.5737		
240		0.5860		

TABLE A LVIII

DECOMPOSITION OF DYSPROSIUM CHROMATE (V) AT 646°C

Time t(mins)	$t^{2.92} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0018		
20		0.0018		
30		0.0018		
40		0.0106		
50		0.0230		
60		0.0478		
70	2.442	0.0903		0.0462
80	3.607	0.1345	0.0626	0.0697
90	5.086	0.1858	0.0892	0.0977
100		0.2389	0.1186	0.1276
110		0.2779	0.1415	0.1502
120		0.3274	0.1724	0.1799
130		0.3681	0.1995	0.2051
140		0.4106	0.2297	0.2323
150		0.4442	0.2551	
160		0.4743	0.2792	
170		0.5062		
180		0.5257		
190		0.5558		
200		0.5664		
210		0.5894		
220		0.6088		
230		0.6177		
240		0.6336		

TABLE A LIX

DECOMPOSITION OF DYSPROSIUM CHROMATE (V) AT 648°C

Time t(mins)	$t^{2.97} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0018		
20		0.0035		
30		0.0123		
40	0.573	0.0350		
50	1.112	0.0648		
60	1.911	0.1156	0.0534	0.0596
70	3.019	0.1734	0.0828	0.0908
80		0.2417	0.1202	0.1292
90		0.2995	0.1547	0.1640
100		0.3555	0.1909	0.1972
110		0.4028	0.2238	0.2272
120		0.4431	0.2544	0.2537
130		0.4851	0.2882	
140		0.5166		
150		0.5377		
160		0.5622		
170		0.5797		
180		0.6060		
190		0.6252		
200		0.6340		
210		0.6497		
220		0.6673		
230		0.6690		
240		0.6830		

TABLE A LX

DECOMPOSITION OF DYSPROSIUM CHROMATE(V) AT 650°C

Time t(mins)	$t^{3.36} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0		
20		0.0035		
30	0.919	0.0158		
40	2.416	0.0404		
50	5.112	0.0877		0.0449
60	9.436	0.1509	0.0712	0.0785
70		0.2193	0.1075	0.1164
80		0.2842	0.1453	0.1540
90		0.3421	0.1818	0.1889
100		0.4000	0.2219	0.2254
110		0.4386	0.2506	
120		0.4737		
130		0.5070		
140		0.5368		
150		0.5596		
160		0.5789		
170		0.6017		
180		0.6211		
190		0.6316		
200		0.6509		
210		0.6667		
220		0.6719		
230		0.6842		
240		0.6982		

TABLE A LXI

DECOMPOSITION OF DYSPROSIUM CHROMATE(V) AT 655°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0		
10	0		
20	0.0035		
30	0.0315		
40	0.0876	0.0399	0.0448
50	0.1646	0.0781	0.0860
60	0.2504	0.1252	0.1342
70	0.3187	0.1668	0.1746
80	0.3835	0.2100	0.2148
90	0.4326	0.2460	
100	0.4816		
110	0.5184		
120	0.5429		
130	0.5674		
140	0.5902		
150	0.6095		
160	0.6287		
170	0.6392		
180	0.6585		
190	0.6725		
200	0.6760		
210	0.6848		
220	0.6970		
230	0.7005		
240	0.7023		

TABLE A LXII

DECOMPOSITION OF DYSPROSIUM CHROMATE(V) AT 660°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0	0		
10	0.0018		
20	0.0160		
30	0.0746	0.0338	0.0380
40	0.1723	0.0820	0.0902
50	0.2682	0.1354	0.1445
60	0.3552	0.1906	0.1970
70	0.4192	0.2360	0.2379
80	0.4725		
90	0.5151		
100	0.5577		
110	0.5950		
120	0.6146		
130	0.6448		
140	0.6536		
150	0.6767		
160	0.6909		
170	0.7034		
180	0.7211		
190	0.7336		
200	0.7389		
210	0.7425		
220	0.7531		
230	0.7638		
240	0.7709		

TABLE A LXIII

DECOMPOSITION OF DYSPROSIUM CHROMATE (V) AT 672°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.0321	0.0140	0.0162
20	0.2121	0.1035	0.1124
30	0.3797	0.2073	0.2124
40	0.4848	0.2880	
50	0.5579		
60	0.6150		
70	0.6613		
80	0.6863		
90	0.7112		
100	0.7273		
110	0.7451		
120	0.7522		
130	0.7629		
140	0.7772		
150	0.7843		
160	0.7914		
170	0.7986		
180	0.8039		
190	0.8039		
200	0.8075		
210	0.8128		
220	0.8182		
230	0.8289		
240	0.8342		

TABLE A LXIV

DECOMPOSITION OF HOLMIUM CHROMATE(V) AT 649°C

Time t(mins)	$t^{3\cdot07} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0		
20		0		
30		0.0018		
40		0.0018		
50		0.0072		
60		0.0107		
70	4.62	0.0161		
80	6.96	0.0215		
90	9.99	0.0340		
100	1.38	0.0501		
110	1.85	0.0626		0.0317
120	2.42	0.0877	0.0399	0.0448
130	3.09	0.1091	0.0500	0.0561
140	3.88	0.1377	0.0645	0.0713
150		0.1628	0.0770	0.0851
160		0.1843	0.0885	0.0967
170		0.2111	0.1032	0.1118
180		0.2343	0.1158	0.1248
190		0.2630	0.1326	0.1414
200		0.2844	0.1453	0.1539
210		0.3095	0.1608	0.1690
220		0.3327	0.1759	0.1830
230		0.3560	0.1911	0.1974
240		0.3739	0.2034	0.2086

TABLE A LXV

DECOMPOSITION OF HOLMIUM CHROMATE (V) AT 655°C

Time t(mins)	$t^{2.61} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0036		
20		0.0072		
30		0.0162		
40		0.0215		
50	0.272	0.0341		
60	0.438	0.0539		
70	0.654	0.0790		
80	0.927	0.1149	0.0531	0.0592
90	1.260	0.1544	0.0730	0.0804
100	1.660	0.2011	0.0976	0.1061
110		0.2478	0.1235	0.1326
120		0.2801	0.1428	0.1516
130		0.3178	0.1662	0.1740
140		0.3501	0.1872	0.1939
150		0.3860	0.2119	
160		0.4183	0.2352	
170		0.4381		
180		0.4650		
190		0.4847		
200		0.5081		
210		0.5242		
220		0.5422		
230		0.5583		
240		0.5745		

TABLE A LXVI

DECOMPOSITION OF HOLMIUM CHROMATE (V) AT 660°C

Time t(mins)	$t^{2.82} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0053		
20		0.0089		
30		0.0107		
40		0.0195		
50	0.618	0.0337		
60	1.034	0.0515		
70	1.597	0.0906		0.0463
80	2.327	0.1314		0.0681
90	3.242	0.1687	0.0802	0.0882
100		0.2114	0.1032	0.1120
110		0.2540	0.1271	0.1362
120		0.2984	0.1538	0.1623
130		0.3304	0.1741	0.1817
140		0.3694	0.2004	0.2059
150		0.3996	0.2217	0.2250
160		0.4281	0.2427	0.2437
170		0.4565	0.2648	
180		0.4831		
190		0.5044		
200		0.5187		
210		0.5382		
220		0.5577		
230		0.5684		
240		0.5826		

TABLE A LXVII

DECOMPOSITION OF HOLMIUM CHROMATE(V) AT 662°C

Time t(mins)	$t^{2\cdot95} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0036		
20		0.0054		
30		0.0108		
40	0.532	0.0306		
50	1.028	0.0576		0.0291
60	1.761	0.1043	0.0476	0.0536
70	2.773	0.1565	0.0742	0.0815
80		0.2140	0.1045	0.1135
990		0.2662	0.1345	0.1433
100		0.3165	0.1653	0.1732
110		0.3579	0.1923	0.1987
120		0.3957	0.2188	0.2227
130		0.4335	0.2467	
140		0.4676		
150		0.4874		
160		0.5126		
170		0.5342		
180		0.5558		
190		0.5719		
200		0.5881		
210		0.6061		
220		0.6241		
230		0.6277		
240		0.6267		

TABLE A LXVIII

DECOMPOSITION OF HOLMIUM CHROMATE (V) AT 665°C

Time t(mins)	$t^{3.03} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0036		
20		0.0108		
30		0.0180		
40	0.715	0.0449		
50	1.406	0.0916	0.0418	0.0468
60	2.443	0.1562	0.0738	0.0815
70		0.2226	0.1093	0.1184
80		0.2873	0.1470	0.1557
90		0.3411	0.1812	0.1883
100		0.3842	0.2106	0.2152
110		0.4273		
120		0.4650		
130		0.4901		
140		0.5206		
150		0.5440		
160		0.5673		
170		0.5835		
180		0.6014		
190		0.6176		
200		0.6212		
210		0.6320		
220		0.6445		
230		0.6553		
240		0.6661		

TABLE A LXIX

DECOMPOSITION OF HOLMIUM CHROMATE (V) AT 668°C

Time t(mins)	$t^{2.48} \times 10^{-3}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0107		
20		0.0285		
30	4.605	0.1032	0.0472	0.0529
40	9.401	0.1993	0.0965	0.1050
50		0.2883	0.1476	0.1563
60		0.3630	0.1959	0.2018
70		0.4235	0.2392	0.2407
80		0.4751	0.2799	
90		0.5214		
100		0.5569		
110		0.5872		
120		0.6139		
130		0.6370		
140		0.6530		
150		0.6584		
160		0.6779		
170		0.6868		
180		0.7011		
190		0.7082		
200		0.7171		
210		0.7313		
220		0.7349		
230		0.7349		
240		0.7420		

TABLE A LXX

DECOMPOSITION OF HOLMIUM CHROMATE AT 670°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0		
10	0.0054		
20	0.0411	0.0182	0.0208
30	0.1232	0.0573	0.0635
40	0.2268	0.1116	0.1206
50	0.3161	0.1650	0.1731
60	0.3857	0.2116	0.2162
70	0.4482	0.2582	
80	0.4911		
90	0.5286		
100	0.5714		
110	0.5946		
120	0.6089		
130	0.6286		
140	0.6482		
150	0.6589		
160	0.6750		
170	0.6839		
180	0.6946		
190	0.7000		
200	0.7036		
210	0.7196		
220	0.7232		
230	0.7286		
240	0.7339		

TABLE A LXXI

DECOMPOSITION OF HOLMIUM CHROMATE(V) AT 675°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10}\frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0	0		
10	0.0054		
20	0.0377	0.0165	0.0189
30	0.1329	0.0618	0.0687
40	0.2496	0.1249	0.1336
50	0.3411	0.1812	0.1883
60	0.4129	0.2311	0.2337
70	0.4684	0.2847	
80	0.5189		
90	0.5566		
100	0.5907		
110	0.6104		
120	0.6391		
130	0.6499		
140	0.6715		
150	0.6822		
160	0.6948		
170	0.7020		
180	0.7145		
190	0.7199		
200	0.7307		
210	0.7325		
220	0.7361		
230	0.7415		
240	0.7478		

TABLE A LXXII

DECOMPOSITION OF HOLMIUM CHROMATE(V) AT 680°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10}\frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0		
10	0.0125		
20	0.0932	0.0425	0.0471
30	0.2401	0.1192	0.1282
40	0.3584	0.1928	0.1989
50	0.4480	0.2582	
60	0.5143		
70	0.5663		
80	0.5968		
90	0.6308		
100	0.6505		
110	0.6738		
120	0.6864		
130	0.6953		
140	0.7115		
150	0.7240		
160	0.7294		
170	0.7401		
180	0.7455		
190	0.7545		
200	0.7563		
210	0.7599		
220	0.7634		
230	0.7670		
240	0.7688		

TABLE A LXXIII

DECOMPOSITION OF HOLMIUM CHROMATE(V) AT 686°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0		
10	0.0145		
20	0.1364	0.0637	0.0706
30	0.2964	0.1526	0.1611
40	0.4145	0.2324	0.2348
50	0.4945	0.2963	
60	0.5509		
70	0.5982		
80	0.6364		
90	0.6600		
100	0.6764		
110	0.6945		
120	0.7073		
130	0.7164		
140	0.7309		
150	0.7400		
160	0.7455		
170	0.7491		
180	0.7509		
190	0.7582		
200	0.7618		
210	0.7673		
220	0.7709		
230	0.7836		
240	0.7873		

TABLE A LXXIV

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 652°C

Time t(mins)	$t^{2.49} \times 10^{-4}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{(1-x)}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0	0	0
10		0.0072	0.0029	0.0037
20		0.0108	0.0047	0.0055
30		0.0126	0.0055	0.0064
40		0.0287	0.0128	0.0145
50	1.700	0.0395	0.0174	0.0200
60	2.677	0.0592	0.0265	0.0301
70	3.929	0.0898	0.0411	0.0460
80	5.479	0.1221	0.0565	0.0630
90	7.345	0.1688	0.0802	0.0883
100	9.550	0.2118	0.1035	0.1121
110		0.2567	0.1287	0.1378
120		0.2980	0.1538	0.1622
130		0.3357	0.1775	0.1850
140		0.3770	0.2054	0.2109
150		0.4057	0.2261	0.2291
160		0.4399	0.2516	0.2517
170		0.4722	0.2777	0.2735
180		0.4955	0.2971	0.2899
190		0.5206	0.3194	0.3076
200		0.5458	0.3428	0.3261
210		0.5655	0.3619	0.3408
220		0.5853	0.3822	0.3561
230		0.6050	0.4034	0.3715
240		0.6176	0.4174	0.3816

TABLE A LXXV

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 659°C

Time t(mins)	$t^{2.51} \times 10^{-4}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0	0	
10		0.0090	0.0037	0.0045
20		0.0144	0.0064	0.0073
30		0.0233	0.0103	0.0120
40		0.0377	0.0165	0.0191
50	1.839	0.0610	0.0274	0.0310
60	2.906	0.0987	0.0453	0.0507
70	4.278	0.1346	0.0630	0.0697
80		0.1813	0.0867	0.0950
90		0.2352	0.1165	0.1253
100		0.2765	0.1405	0.1495
110		0.3214	0.1685	0.1762
120		0.3591	0.1931	0.1994
130		0.4057	0.2261	0.2291
140		0.4363	0.2490	0.2493
150		0.4614	0.2688	0.2663
160		0.4919	0.2941	0.2871
170		0.5206	0.3194	0.3076
180		0.5440	0.3410	0.3247
190		0.5709	0.3674	
200		0.5925	0.3899	
210		0.6158	0.4155	
220		0.6266		
230		0.6427		
240		0.6607		

TABLE A LXXVI

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 661°C

Time t(mins)	$t^{2.98} \times 10^{-4}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0	0	0
10		0.0090	0.0037	0.0045
20		0.0108	0.0047	0.0055
30	2.523	0.0288	0.0128	0.0145
40	5.947	0.0665	0.0298	0.0340
50	11.560	0.1385	0.0649	0.0717
60		0.2086	0.1018	0.1103
70		0.2770	0.1409	0.1498
80		0.3435	0.1826	0.1898
90		0.3957	0.2188	0.2226
100		0.4424	0.2536	0.2532
110		0.4910	0.2934	0.2866
120		0.5288	0.3267	0.3135
130		0.5576	0.3541	
140		0.5863	0.3832	
150		0.6205	0.4208	
160		0.6385	0.4418	
170		0.6619		
180		0.6763		
190		0.6978		
200		0.7140		
210		0.7266		
220		0.7464		
230		0.7536		
240		0.7662		

TABLE A LXXVII

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 667°C

Time t(mins)	$t^{2.88} \times 10^{-4}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0	0	0
10		0.0036	0.0017	0.0018
20	0.558	0.0145	0.0064	0.0073
30	1.795	0.0508	0.0229	0.0258
40	4.111	0.1125	0.0518	0.0581
50		0.1960	0.0948	0.1034
60		0.2704	0.1370	0.1460
70		0.3430	0.1824	0.1894
80		0.3993	0.2214	0.2250
90		0.4555	0.2641	0.2621
100		0.4991	0.3002	0.2921
110		0.5463	0.3432	
120		0.5771	0.3738	
130		0.6044	0.4028	
140		0.6334		
150		0.6570		
160		0.6770		
170		0.6915		
180		0.7132		
190		0.7278		
200		0.7423		
210		0.7586		
220		0.7677		
230		0.7768		
240		0.7822		

TABLE A LXXVIII

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 670°C

Time t(mins)	$t^{2.62} \times 10^{-3}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0		0	0	0
10		0.0090	0.0037	0.0045
20	2.524	0.0306	0.0136	0.0155
30	7.288	0.0883	0.0403	0.0451
40		0.1730	0.0823	0.0907
50		0.2559	0.1284	0.1374
60		0.3412	0.1812	0.1884
70		0.4126	0.2309	0.2336
80		0.4703	0.2761	0.2721
90		0.5225	0.3209	0.2921
100		0.5622	0.3587	0.3090
110		0.6036	0.4019	
120		0.6288	0.4305	
130		0.6577		
140		0.6829		
150		0.6991		
160		0.7135		
170		0.7315		
180		0.7423		
190		0.7514		
200		0.7658		
210		0.7766		
220		0.7874		
230		0.7892		
240		0.7982		

TABLE A LXXIX

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 675°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10}\frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.0109	0.0047	0.0055
20	0.0364	0.0161	0.0185
30	0.1129	0.0518	0.0583
40	0.2204	0.1082	0.1171
50	0.3188	0.1668	0.1748
60	0.3971	0.2199	0.2236
70	0.4699	0.2756	0.2718
80	0.5246	0.3228	
90	0.5756	0.3722	
100	0.6175		
110	0.6503		
120	0.6812		
130	0.7049		
140	0.7250		
150	0.7468		
160	0.7650		
170	0.7814		
180	0.7960		
190	0.8015		
200	0.8124		
210	0.8197		
220	0.8342		
230	0.8434		
240	0.8506		

TABLE A LXXX

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 677°C

Time t(mins)	Fraction Decomposed (x)	$Log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.0164	0.0072	0.0083
20	0.0655	0.0294	0.0335
30	0.1727	0.0823	0.0905
40	0.2982	0.1538	0.1622
50	0.3945	0.2180	0.2218
60	0.4764	0.2810	0.2763
70	0.5364	0.3336	0.3190
80	0.5873	0.3843	
90	0.6345		
100	0.6655		
110	0.6909		
120	0.7200		
130	0.7327		
140	0.7564		
150	0.7691		
160	0.7800		
170	0.7982		
180	0.8036		
190	0.8164		
200	0.8182		
210	0.8291		
220	0.8455		
230	0.8509		
240	0.8527		

TABLE A LXXXI

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 680°C

Time t(mins)	Fraction Decomposed (x)	$Log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.0216	0.0094	0.0110
20	0.0991	0.0453	0.0510
30	0.2288	0.1130	0.1217
40	0.3477	0.1855	0.1924
50	0.4523	0.2615	0.2598
60	0.5243	0.3226	0.3182
70	0.5802	0.3770	
80	0.6342		
90	0.6739		
100	0.7009		
110	0.7351		
120	0.7441		
130	0.7694		
140	0.7784		
150	0.7928		
160	0.8072		
170	0.8144		
180	0.8270		
190	0.8288		
200	0.8378		
210	0.8432		
220	0.8486		
230	0.8577		
240	0.8613		

TABLE A LXXXII

DECOMPOSITION OF ERBIUM CHROMATE(V) AT 690°C

Time t(mins)	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0	0	0	0
10	0.0543	0.0241	0.0277
20	0.2559	0.1284	0.1374
30	0.4265	0.2415	0.2426
40	0.5417	0.3389	
50	0.6178	0.4176	
60	0.6757		
70	0.7138		
80	0.7482		
90	0.7772		
100	0.7899		
110	0.8134		
120	0.8225		
130	0.8315		
140	0.8424		
150	0.8551		
160	0.8569		
170	0.8696		
180	0.8714		
190	0.8750		
200	0.8768		
210			
220			
230			
240			

TABLE A LXXXIII

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 628°C

Time t(mins)	$t^{3\cdot23} \times 10^{-7}$	Fraction Decomposed (x)
0		0
10		0
20		0
30		0
40		0.0019
50		0.0019
60		0.0057
70		0.0076
80		0.0095
90		0.0133
100		0.0170
110		0.0170
120		0.0189
130		0.0208
140		0.0265
150	1.090	0.0360
160	1.343	0.0417
170	1.633	0.0530
180	1.966	0.0625
190	2.342	0.0739
200	2.764	0.0852
210	3.236	0.1023
220	3.761	0.1212
230	4.342	0.1364
240	4.984	0.1591

TABLE A LXXXIV

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 634°C

Time t(mins)	$t^{2.88} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0		
20		0		
30		0.0038		
40		0.0057		
50		0.0114		
60		0.0170		
70		0.0208		
80		0.0265		
90		0.0436		
100	5.649	0.0568		
110	7.432	0.0701		
120	9.532	0.0928		
130	12.010	0.1136		
140	14.870	0.1477		0.0768
150	18.130	0.1761	0.0842	0.0923
160	21.830	0.2102	0.1025	0.1113
170		0.2462	0.1229	0.1318
180		0.2727	0.1383	0.1472
190		0.3049	0.1580	0.1663
200		0.3409	0.1810	0.1882
210		0.3636	0.1962	0.2023
220		0.3977	0.2201	0.2239
230		0.4242	0.2397	0.2412
240		0.4508	0.2603	0.2589

TABLE A LXXXV

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 637°C

Time t(mins)	$t^{2.57} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0057		
20		0.0152		
30		0.0210		
40		0.0248		
50		0.0267		
60		0.0362		
70		0.0419		
80	0.768	0.0476		
90	1.039	0.0667		
100	1.361	0.0895		
110	1.739	0.1143		
120	2.172	0.1371		
130	2.669	0.1733		0.0908
140	3.228	0.1981		0.1045
150		0.2343	0.1158	0.1250
160		0.2686	0.1358	0.1448
170		0.2933	0.1507	0.1593
180		0.3295	0.1735	0.1812
190		0.3657	0.1978	0.2036
200		0.3962	0.2191	0.2230
210		0.4343	0.2475	0.2479
220		0.4610	0.2684	0.2658
230		0.4857	0.2887	0.2829
240		0.5143	0.3137	

TABLE A LXXXVI

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 641°C

Time t(mins)	$t^{2.81} \times 10^{-5}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0		
20		0.0076		
30		0.0134		
40		0.0153		
50		0.0210		
60		0.0382		
70	1.537	0.0574		
80	2.237	0.0918		
90	3.114	0.1224		
100	4.188	0.1663	0.0789	0.0869
110		0.2065	0.1004	0.1092
120		0.2486	0.1242	0.1332
130		0.2945	0.1513	0.1601
140		0.3403	0.1807	0.1878
150		0.3824	0.2092	0.2141
160		0.4168	0.2342	0.2363
170		0.4532	0.2622	0.2605
180		0.4876	0.2904	0.2842
190		0.5124	0.3120	
200		0.5392	0.3365	
210		0.5621		
220		0.5813		
230		0.6023		
240		0.6252		

TABLE A LXXXVII

DECOMPOSITION OF YTTERBIUM CHROMATE (V) AT 647°C

Time t (mins)	$t^{2.86} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$\sqrt{1-(1-x)^{\frac{1}{2}}}$
0		0		
10		0.0039		
20		0.0077		
30		0.0097		
40		0.0135		
50		0.0309		
60	1.238	0.0658		
70	1.925	0.1044		0.0536
80	2.821	0.1470	0.0690	0.0764
90		0.1954	0.0944	0.1030
100		0.2437	0.1212	0.1303
110		0.2921	0.1501	0.1586
120		0.3404	0.1807	0.1878
130		0.3810	0.2080	0.2132
140		0.4217	0.2377	0.2395
150		0.4623	0.2695	0.2667
160		0.4990	0.3002	
170		0.5203	0.3192	
180		0.5571	0.3537	
190		0.5764		
200		0.5996		
210		0.6228		
220		0.6460		
230		0.6576		
240		0.6731		

TABLE A LXXXVIII

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 650°C

Time t (mins)	$t^{2.46} \times 10^{-4}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0		0		
10		0.0116		
20		0.0193		
30		0.0309		
40	0.880	0.0561		
50	1.524	0.0928		
60	2.387	0.1509	0.0712	0.0785
70	3.488	0.2147	0.1048	0.1138
80		0.2805	0.1430	0.1518
90		0.3462	0.1847	0.1914
100		0.4062	0.2264	0.2294
110		0.4681	0.2742	0.2707
120		0.5184	0.3173	0.3060
130		0.5571	0.3537	
140		0.5899		
150		0.6170		
160		0.6499		
170		0.6731		
180		0.6944		
190		0.7099		
200		0.7311		
210		0.7466		
220		0.7563		
230		0.7717		
240		0.7737		

TABLE A LXXXIX

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 652°C

Time t (mins)	$t^{2.67} \times 10^{-4}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0		0		
10		0.0098		
20		0.0234		
30		0.0313		
40	1.874	0.0508		
50	3.398	0.0879		
60	5.528	0.1523	0.0719	0.0793
70	8.365	0.2207	0.1082	0.1172
80		0.2852	0.1459	0.1545
90		0.3574	0.1920	0.1982
100		0.4160	0.2335	0.2358
110		0.4727	0.2779	0.2738
120		0.5156	0.3147	
130		0.5566		
140		0.5996		
150		0.6328		
160		0.6602		
170		0.6875		
180		0.7109		
190		0.7324		
200		0.7500		
210		0.7617		
220		0.7734		
230		0.7852		
240		0.7871		

TABLE A XC

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 654°C

Time t (mins)	$t^{2.86} \times 10^{-4}$	Fraction Decomposed (x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0097		
20		0.0135		
30		0.0271		
40	3.833	0.0600		
50	7.258	0.1199		0.0619
60	12.230	0.1876	0.0902	0.0987
70		0.2631	0.1326	0.1416
80		0.3346	0.1769	0.1843
90		0.3946	0.2180	0.2219
100		0.4565	0.2648	0.2628
110		0.5029	0.3036	
120		0.5513	0.3481	
130		0.5822		
140		0.6248		
150		0.6596		
160		0.6789		
170		0.6925		
180		0.7176		
190		0.7273		
200		0.7447		
210		0.7582		
220		0.7776		
230		0.7853		
240		0.8008		

TABLE A XCI

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 661°C

Time t (mins)	$t^{2.87} \times 10^{-4}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0077		
20		0.0232		
30	1.759	0.0560		
40	4.022	0.1274		0.0659
50		0.2220	0.1089	0.1180
60		0.3089	0.1605	0.1687
70		0.3977	0.2201	0.2239
80		0.4826	0.2863	0.2807
90		0.5463	0.3432	
100		0.5907		
110		0.6351		
120		0.6795		
130		0.7027		
140		0.7278		
150		0.7568		
160		0.7741		
170		0.7838		
180		0.8012		
190		0.8147		
200		0.8243		
210		0.8263		
220		0.8436		
230		0.8456		
240		0.8514		

TABLE A XCII

DECOMPOSITION OF YTTERBIUM CHROMATE(V) AT 670°C

Time t (mins)	$t^{2.50} \times 10^{-3}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0138		
20	1.810	0.0494		
30	4.997	0.1344	0.0626	0.0696
40		0.2609	0.1313	0.1403
50		0.3854	0.2113	0.2160
60		0.4862	0.2891	0.2832
70		0.5692	0.3657	
80		0.6304		
90		0.6858		
100		0.7253		
110		0.7490		
120		0.7747		
130		0.7964		
140		0.8241		
150		0.8399		
160		0.8478		
170		0.8636		
180		0.8755		
190		0.8834		
200		0.8854		
210		0.8913		
220		0.8992		
230		0.8992		
240		0.9111		

TABLE A XCIII

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 651°C

Time t (mins)	$t^{2.70} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0039		
20		0.0065		
30		0.0091		
40		0.0091		
50		0.0104		
60		0.0169		
70		0.0195		
80		0.0221		
90		0.0286		
100		0.0351		
110	3.249	0.0455		
120	4.110	0.0545		
130	5.099	0.0675		
140	6.230	0.0831		
150	7.508	0.0987		
160	8.935	0.1195		0.0617
170	10.520	0.1390	0.0649	0.0721
180	12.280	0.1649	0.0781	0.0861
190	14.220	0.1922	0.0927	0.1014
200	16.320	0.2169	0.1062	0.1151
210		0.2416	0.1202	0.1292
220		0.2662	0.1345	0.1433
230		0.2961	0.1526	0.1610
240		0.3182	0.1665	0.1744

TABLE A XCIV

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 656°C

Time t(mins)	$t^{2.54} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0065		
20		0.0091		
30		0.0117		
40		0.0144		
50		0.0196		
60		0.0222		
70		0.0261		
80		0.0300		
90	0.920	0.0392		
100	1.202	0.0522		
110	1.532	0.0627		
120	1.911	0.0809		
130	2.341	0.0966		
140	2.826	0.1201		
150	3.367	0.1449		0.0753
160	3.967	0.1658	0.0789	0.0867
170	4.626	0.1958	0.0944	0.1031
180	5.352	0.2272	0.1120	0.1210
190	6.141	0.2559	0.1284	0.1374
200		0.2820	0.1440	0.1528
210		0.3159	0.1650	0.1729
220		0.3355	0.1775	0.1849
230		0.3655	0.1976	0.2034
240		0.3916	0.2159	0.2200

TABLE A XCV

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 658°C

Time t (mins)	$t^{2.62} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0065		
20		0.0065		
30		0.0065		
40		0.0078		
50		0.0156		
60		0.0209		
70		0.0261		
80	0.948	0.0404		
90	1.289	0.0522		
100	1.698	0.0730		
110	2.179	0.0887		
120	2.736	0.1160		
130	3.371	0.1421		0.0738
140	4.094	0.1708		0.0895
150	4.904	0.1982	0.0958	0.1046
160		0.2360	0.1168	0.1260
170		0.2660	0.1341	0.1433
180		0.2986	0.1541	0.1627
190		0.3312	0.1747	0.1823
200		0.3638	0.1965	0.2023
210		0.3924	0.2164	0.2206
220		0.4263	0.2412	0.2427
230		0.4550	0.2637	0.2618
240		0.4785	0.2828	0.2779

TABLE A XCVI

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 660°C

Time t (mins)	$t^{2.76} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0052		
20		0.0079		
30		0.0092		
40		0.0144		
50	0.489	0.0223		
60	0.809	0.0366		
70	1.237	0.0589		
80	1.788	0.0864		
90	2.475	0.1178		
100	3.311	0.1571		0.0819
110	4.308	0.2003	0.0969	0.1059
120		0.2435	0.1212	0.1302
130		0.2866	0.1467	0.1555
140		0.3312	0.1747	0.1823
150		0.3704	0.2009	0.2066
160		0.4045	0.2251	0.2284
170		0.4398	0.2516	
180		0.4725	0.2779	
190		0.5065	0.3067	
200		0.5380	0.3353	
210		0.5628	0.3593	
220		0.5877	0.3847	
230		0.6086		
240		0.6322		

TABLE A XCVII

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 662°C

Time t (mins)	$t^{3\cdot22} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$\left[1-(1-x)^{\frac{1}{2}}\right]$
0		0		
10		0.0013		
20		0.0052		
30		0.0052		
40		0.0118		
50	2.956	0.0236		
60	5.319	0.0419		
70	8.734	0.0746		
80	13.43	0.1060		0.0546
90	19.61	0.1610		0.0840
100		0.2068	0.1007	0.1094
110		0.2605	0.1309	0.1402
120		0.3050	0.1580	0.1663
130		0.3482	0.1858	0.1928
140		0.3953	0.2186	0.2225
150		0.4332	0.2465	0.2472
160		0.4738	0.2788	
170		0.5079	0.3079	
180		0.5353	0.3328	
190		0.5589		
200		0.5851		
210		0.6086		
220		0.6283		
230		0.6479		
240		0.6662		

TABLE A XCVIII

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 665°C

Time t(mins)	$t^{3\cdot13} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0052		
20		0.0065		
30		0.0092		
40	1.034	0.0196		
50	2.079	0.0405		
60	3.680	0.0719		
70	5.960	0.1163		0.0601
80	9.051	0.1752	0.0835	0.0920
90		0.2314	0.1142	0.1234
100		0.2941	0.1513	0.1597
110		0.3477	0.1855	0.1924
120		0.3961	0.2191	0.2231
130		0.4405	0.2521	
140		0.4824	0.2860	
150		0.5190		
160		0.5516		
170		0.5830		
180		0.6039		
190		0.6301		
200		0.6497		
210		0.6627		
220		0.6837		
230		0.6928		
240		0.6993		

TABLE A XCIX

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 670°C

Time t(mins)	$t^{3\cdot12} \times 10^{-5}$	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0		0		
10		0.0026		
20		0.0065		
30		0.0248		
40	0.997	0.0561		
50	1.999	0.1082		0.0557
60	3.532	0.1799	0.0859	0.0945
70		0.2568	0.1290	0.1380
80		0.3325	0.1756	0.1830
90		0.3963	0.2191	0.2231
100		0.4563	0.2646	
110		0.5059	0.3062	
120		0.5476		
130		0.5841		
140		0.6141		
150		0.6441		
160		0.6649		
170		0.6845		
180		0.7027		
190		0.7145		
200		0.7275		
210		0.7405		
220		0.7523		
230		0.7653		
240		0.7718		

TABLE A C

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 680°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0		
10	0.0026		
20	0.0092		
30	0.0512		
40	0.1340	0.0626	0.0695
50	0.2339	0.1155	0.1248
60	0.3325	0.1756	0.1830
70	0.4218	0.2380	0.2397
80	0.4901	0.2925	
90	0.5545	0.3512	
100	0.5992		
110	0.6321		
120	0.6610		
130	0.6886		
140	0.7096		
150	0.7254		
160	0.7424		
170	0.7530		
180	0.7648		
190	0.7753		
200	0.7819		
210	0.7911		
220	0.8003		
230	0.8068		
240	0.8147		

TABLE A CI

DECOMPOSITION OF YTTRIUM CHROMATE(V) AT 701°C

Time t(mins)	Fraction Decomposed(x)	$\log_{10} \frac{1}{1-x}$	$[1-(1-x)^{\frac{1}{2}}]$
0	0	0	0
10	0.0354	0.0157	0.0178
20	0.2412	0.1199	0.1288
30	0.4417	0.2531	0.2529
40	0.5714		
50	0.6435		
60	0.6907		
70	0.7261		
80	0.7536		
90	0.7693		
100	0.7824		
110	0.7969		
120	0.8073		
130	0.8126		
140	0.8204		
150	0.8257		
160	0.8349		
170	0.8375		
180	0.8453		
190	0.8493		
200	0.8519		
210	0.8571		
220	0.8637		
230	0.8676		
240	0.8716		

TABLE A CII

I.R. SPECTRA OF SOME PARTIALLY DECOMPOSED SAMPLES OF PRASEODYMIUM CHROMATE (VI)

$Pr_2(CrO_4)_3$	x = 0.38	$PrCrO_4$	x = 0.47	x = 0.59	x = 0.84	$PrCrO_3$
1005 m.	1005 w.					
940 s.	940 m.		955 m.	950 w.	950 w.	
		838 w.sh.				
790 s.br.		788 m.				
	720 m.	732 s.	720 s.	715 m.		
				640 m.	630 s.	610 s.
455 m.						457 m.
435 m.	415 m.		415 m.	410 m.	410 m.	423 m.

TABLE A CIII

X-RAY DIFFRACTION PATTERNS OF PARTIALLY DECOMPOSED SAMPLES OF PRASEODYMIUM CHROMATE(V)

$PrCrO_4$		x = 0.45		x = 0.55		x = 0.80		x = 1.00		$PrCrO_3$	
	Int.	dA°	Int.	dA°	Int.	dA°	Int.	dA°	Int.	dA°	Int.
		3.85	33	3.83	25	3.85	24	3.85	22	3.85	18
9	100	3.66	46	3.66	39	3.68	15				
5	26	3.35	25								
5	39	3.14	35								
3	43	2.92	27								
		2.730	100	2.730	100	2.659	100	2.630	100	2.722	100
		2.227	25	2.227	23	2.227	23	2.227	20	2.222	22
		1.933	34	1.929	37	1.933	40	1.933	36	1.929	37
		1.876	43	1.880	31	1.876	20	1.873	16	1.873	12

Note:- Only those lines at $PrCrO_4$ and $PrCrO_3$ required to make assignments for the partially decomposed samples are shown here.

TABLE A CIV

X-RAY DIFFRACTION PATTERNS OF PARTIALLY DECOMPOSED SAMPLES OF GADOLINIUM CHROMATE(V)

$GdCrO_4$		x = 0.82		x = 0.93		$GdCrO_3$	
dA°	Int.	dA°	Int.	dA°	Int.	dA°	Int.
		3.78	24	3.78	24	3.82	21
3.59	100	3.60	10				
				3.40	22	3.40	26
		2.722	34	2.763	38	2.746	22
		2.683	100	2.690	100	2.698	100
		2.652	65	2.652	41	2.652	44
				2.585	20	2.593	27
				2.176	21	2.161	20
		1.903	36	1.907	42	1.907	56
				1.852	26	1.831	24

Note:- Only those lines at $GdCrO_4$ and $GdCrO_3$ required to make assignments for the partially decomposed samples are shown here.

TABLE A CV

X-RAY DIFFRACTION PATTERNS OF PARTIALLY DECOMPOSED SAMPLES OF TERBIUM CHROMATE(V)

$TbCrO_4$		x = 0.20		x = 0.55		x = 0.80		x = 1.00		$TbCrO_3$	
dA	Int.	dA	Int.	dA	Int.	dA	Int.	dA	Int.	dA	Int.
4.74	27	4.72	31	4.72	24						
				3.78	19	3.82	23	3.80	22	3.80	24
3.60	100	3.56	100	3.56	60						
				3.41	21	3.40	19	3.40	22	3.39	15
2.90	15	2.858	20								
				2.746	28	2.746	27	2.746	25	2.746	27
				2.690	100	2.683	100	2.690	100	2.675	100
2.675	78	2.667	91	2.659	41	2.652	37				
				2.629	22	2.637	33	2.637	31	2.637	36
				2.593	17	2.585	21	2.585	16	2.585	17
2.535	27	2.529	22	2.529	24						
2.362	12	2.350	23								
2.233	20	2.227	24	2.227	16	2.227	13	2.233	11	2.217	17
				2.171	17	2.166	21	2.171	17	2.166	23
								2.068	11	2.098	15
				1.910	23	1.907	29	1.910	30	1.907	26
1.891	13	1.899	29	1.891	22	1.895	22	1.891	17	1.888	36
		1.863	19	1.859	20	1.859	22	1.863	16	1.855	24
						1.848	24	1.852	15	1.848	25
1.841	58	1.834	75	1.841	39	1.838	19				
1.791	24	1.791	35	1.787	21						

TABLE A CVI

X-RAY DIFFRACTION PATTERNS OF PARTIALLY DECOMPOSED SAMPLES OF DYSPROSIUM CHROMATE(V).

$DyCrO_4$		x = 0.40		x = 0.75		x = 0.90		$DyCrO_3$	
dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.
4.65	40	4.58	46						
		3.74	33	3.75	26	3.75	18	3.75	21
3.56	100	3.53	91	3.53	20				
				3.36	23	3.37	21	3.39	25
				3.19	21	3.14	20	3.06	61
				2.738	26	2.738	27	2.730	25
		2.675	98	2.659	100	2.659	100	2.667	100
2.659	75	2.652	100						
		2.614	31	2.614	33	2.614	35	2.621	38
2.515	32	2.515	32						
2.217	27	2.215	23	2.212	21				
2.002	23	2.002	32						
				1.895	31	1.895	32	1.899	26
				1.824	26	1.834	18	1.841	32
1.824	68	1.827	66						
1.781	21	1.790	43						

TABLE A CVII

X-RAY DIFFRACTION PATTERNS OF PARTIALLY DECOMPOSED SAMPLES OF HOLMIUM CHROMATE (V)

$HoCrO_4$		x = 0.38		x = 0.58		x = 0.77		x = 1.00		HoCrO	
dA	Int.	dA	Int.	dA	Int.	dA	Int.	dA	Int.	dA	I
4.67	27	4.72	27	4.69	10						
		3.87	19	3.78	20	3.78	17	3.77	16	3.78	
3.55	100	3.56	92	3.55	48	3.55	14				
		3.40	15	3.40	23	3.40	19	3.39	25	3.36	
2.83	10	2.81	28								
				2.771	23	2.771	20	2.754	22	2.754	
		2.683	100	2.675	100	2.683	100	2.667	100	2.667	1
2.652	65	2.660	92								
				2.621	30	2.621	27	2.614	29	2.614	
2.522	18	2.522	21	2.515	10						
2.217	14	2.227	20	2.222	14	2.227	14				
		2.098	13	2.094	10	2.098	12	2.090	14	2.076	
1.998	10	2.002	14								
		1.903	27	1.903	26	1.899	25	1.899	27	1.899	
1.888	12	1.888	29	1.884	24	1.888	24	1.880	22	1.873	
				1.848	18	1.845	15	1.841	17	1.834	
1.828	54	1.831	55	1.824	30						
1.781	17	1.778	22								

TABLE A CVIII

X-RAY DIFFRACTION PATTERNS OF PARTIALLY DECOMPOSED SAMPLES OF ERBIUM CHROMATE (V)

$ErCrO_4$		x = 0.62		x = 0.80		x = 1.00		$ErCrO_3$	
dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.
4.68	29	4.65	14						
		3.72	24	3.75	29	3.75	22	3.76	22
3.55	100	3.49	31	3.51	9				
		3.35	29	3.35	24	3.35	25	3.38	21
2.650	77	2.644	100	2.652	100	2.644	100	2.667	80
		2.593	37	2.593	32	2.593	27	2.587	15
				2.243	11	2.238	8	2.251	11
2.212	20	2.212	15	2.212	10	2.212	9		
		2.131	18	2.131	13	2.131	15	2.143	12
		1.888	26	1.884	25	1.884	20	1.877	17
1.877	15	1.876	25						
		1.831	24	1.831	20	1.831	16	1.837	13
1.821	58	1.814	24	1.794	7			1.814	9

TABLE A CIX

X-RAY DIFFRACTION PATTERNS OF PARTIALLY DECOMPOSED SAMPLES OF YTTERBIUM CHROMATE (V)

$YbCrO_4$		x = 0.16		x = 0.55		x = 0.85		x = 1.00		$YbCrO_3$	
dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	In
4.67	34	4.69	40	4.67	31						
		3.78	11	3.83	28	3.77	31	3.78	28	3.77	2
3.53	100	3.55	100	3.52	77	3.53	16				
		3.33	11	3.37	31	3.37	32	3.37	26	3.37	2
		3.03	19							3.01	8
				2.754	25	2.754	27	2.754	21	2.754	2
		2.652	75	2.659	100	2.667	100	2.667	100	2.659	10
						2.217	11	2.222	8	2.217	1
						2.131	13	2.136	15	2.136	1
						2.083	13	2.087	11	2.071	1
1.990	14	1.994	13								
						1.891	22	1.895	18	1.888	2
1.870	20	1.873	14	1.880	22	1.876	19	1.876	17	1.870	2
				1.848	23	1.852	13	1.852	13	1.854	5
1.810	67	1.817	51	1.810	45						
1.765	21	1.765	17	1.759	17						

TABLE A CX

X-RAY DIFFRACTION PATTERNS OF PARTIALLY DECOMPOSED SAMPLES OF YTTRIUM CHROMATE(V)

$YCrO_4$		x = 0.32		x = 0.48		x = 0.70		x = 1.00		$YCrO_3$	
dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	Int.	dÅ	I
								3.75	9	3.74	
3.53	100	3.53	100	3.55	65	3.55	22				
		3.39	20	3.39	15	3.39	21	3.37	22	3.37	
		2.754	20	2.746	25	2.754	23	2.746	24	2.754	
2.64	68	2.667	85	2.667	100	2.675	100	2.675	100	2.675	
		2.629	34	2.621	40	2.614	28	2.607	29	2.621	
2.509	21	2.509	20								
						2.222	10	2.141	10	2.146	
2.206	13	2.212	23								
						2.098	12	2.087	14	2.094	
				1.899	30	1.899	25	1.899	25	1.903	
		1.884	29	1.884	27	1.884	18	1.884	21	1.880	
						1.841	16	1.841	15	1.845	
1.820	56	1.820	62	1.820	40	1.820	11				
1.775	20	1.775	27	1.772	16	1.778	7				

TABLE A CXI

I. R. ABSORPTION MAXIMA (cm^{-1}) FOR SAMPLES OF PRASEODYMIUM CHROMATE(V) DECOMPOSED AT DIFFERENT TEMPERATURES (K Br disk)

. $PrCrO_4$	x = 0.45	x = 0.55	x = 0.80	x = 1.00	. $PrCrO_3$
838 w.sh.	838 w.sh.	838 w.sh.			
788 m.br.	790 m.	799 m.br.			
732 s.	730 s.br.	730 m.br.			
	580 s.br.	620 m.br.	620 m.br.	620 s.br.	
		580 s.br.	580 s.br.	582 s.br.	610s.v.br.
	490 w.sh.	490 w.sh.	490 w.sh.	486 m.sh.	488 m.sh.
	445 w.sh.	435 m. sh.	454 m.	454 m.	457 m.
	420 m.br.	424 m.br.	422 m.br.	422 m.br.	423 m.br.

TABLE A CXII

I. R. ABSORPTION MAXIMA (cm^{-1}) FOR SAMPLES OF GADOLINIUM CHROMATE(V) DECOMPOSED AT DIFFERENT TEMPERATURES (K Br disk)

. $GdCrO_4$	x = 0.82	x = 0.93	$GdCrO_3$
943 w.	940 w.		
861 w.	864 w.		
838 w.			
770 s.	776 w.	775 v.w.	
	577 s.v.br.	577 s.v.br.	585 s.v.br.
540 w.			
	510 m.br.	510 m.br.	513 m.br.
	472 m.br.	477 m.br.	480 m.br.

TABLE A CXIII

I. R. ABSORPTION MAXIMA (cm^{-1}) FOR SAMPLES OF TERBIUM CHROMATE(V)

DECOMPOSED AT DIFFERENT TEMPERATURES (K Br disk)

$TbCrO_4$	x = 0.20	x = 0.55	x = 0.80	x = 1.00	$TbCrO_3$
866 w.sh.	864 w.sh.	865 w.sh.			
838 w.sh.	837 w.sh.	842 w.sh.			
799 s.	780 s.v.br.	775 m.br.	773 v.w.		
				610 s.br.	611 m.br.
	576 w.	578 m.	578 s.	580 s.	586 s.br.
	560 v.w.sh.	562 w.sh.	563 w.sh	565 w.sh.	568 w.sh.
546 w.					
		516 w.	519 w.	519 w.	521 w.
	473 w.br.	482 m.br.	480 m.br.	482 m.br.	487 m.br.
		440 w.	438 w.	440 m.	443 m.
		427 w.	428 w.	430 w.sh.	

TABLE A CXIV

I. R. ABSORPTION MAXIMA (cm^{-1}) FOR SAMPLES OF DYSPROSIUM CHROMATE(V) DECOMPOSED AT DIFFERENT TEMPERATURES (K Br disk)

$DyCrO_4$	x = 0.40	x = 0.75	x = 1.00	$DyCrO_3$
950 w.sh.	950 w.sh.			
860 w.sh.	860 w.sh			
777 s.	775 s.	775 w.br.		
		608 m.br.	611 s.br.	612 s.br.
	580 m.	580 s.br.	584 s.br.	580 s.v.br.
	566 v.w.sh.	570 w.sh.	567 w.sh.	568 w.sh.
545 w.				
	521 v.w.	524 w.	525 w.	525 w.
	481 m.br.	485 m.br.	485 m.br.	483 m. br.
	440 w.	441 w.	442 m.br.	442m.

TABLE A CXV

I. R. ABSORPTION MAXIMA (cm^{-1}) FOR SAMPLES OF HOLMIUM CHROMATE (V) DECOMPOSED AT DIFFERENT TEMPERATURES (K Br disk)

$HoCrO_4$	x = 0.38	x = 0.58	x = 0.77	x = 1.00	$HoCrO_3$
835 w.sh.	832 w.sh.	837 w.sh.			
780 s.	780 s.	773 m.br.	773 w.		
			622 m.br.	621 m.br.	620 m.br.
	582 m.br.	582 m.br.	581 s.br.	580 s.br.	584 s.br.
		567 w.sh.	566 w.sh.	566 w.sh.	570 w.sh.
		526 v.wk.	526 w.	524 w.	526 w.
					510 w.
	478 w.br.	484 m.br.	485 m.br.	486 m.br.	492 m.br.
		435 w.br.	434 m.br.	433 m.br.	435 m.br.

TABLE A CXVI

I. R. ABSORPTION MAXIMA (cm^{-1}) FOR SAMPLES OF ERBIUM CHROMATE(V) DECOMPOSED AT DIFFERENT TEMPERATURES (K Br disk)

$ErCrO_4$	x = 0.62	x = 0.80	x = 1.00	$ErCrO_3$
836 w.sh.				
780 s.br.	780 m.	770 w.sh.		
	613 m.br.	620 m.br.	616 m.br.	608 m.br.
	578 s.br.	585 s.br.	587 s.br.	584 s.br.
	565 w.sh.	572 w.sh.	572 w.sh.	572 w.sh.
	535 w.	533 w.	535 w.	532 w.
	483 m.br.	490 m.br.	492 m.br.	496 m.br.
	436 m.br.	436 m.br.	438 m.br.	438 m.br.

TABLE A CXVII

I. R. ABSORPTION MAXIMA (cm^{-1}) FOR SAMPLES OF YTTERBIUM CHROMATE(V) DECOMPOSED AT DIFFERENT TEMPERATURES (K Br disk)

$YbCrO_4$	x = 0.16	x = 0.55	x = 0.85	x = 1.00	$YbCrO_3$
895 w.sh.	852 w.sh.	846 w.sh.			
780 s.br.	782 s.br.	786 s.br.	785 w.br.		
		610 m.	620 s.br.	620 s.br.	619 s.br.
	584 w.	588 m.br.	583 s.br.	591 s.br.	588 s.br.
		572 w.sh.	573 w.sh.	5702w.sh.	565 w.sh
				540 w.	532 m.
				513 m.	510 m.
	490 w.	492 m.br.	490 s.br.	496 s.br.	492 s.
	438 w.	440 m.br.	440 m.br.	443 m.br.	442 m.

TABLE A CXVIII

I. R. ABSORPTION MAXIMA (cm^{-1}) FOR SAMPLES OF YTTRIUM CHROMATE(V) DECOMPOSED AT DIFFERENT TEMPERATURES

$YCrO_4$	x = 0.32	x =0.48	x = 0.70	x = 1.00	$YCrO_3$
850 w.sh.	850 w.sh.	843 w.sh.			
780 s.	785 s.	782 m.	780 w.br.		
		619 m.br.	621 m.br.	623 s.br.	619 s.br.
	583 m.br.	583 s.br.	582 s.br.	584 s.br.	588 s.br.
	572 w.sh.	571 w.sh.	572 w.sh.	572 w.sh.	565 w.sh.
	582 w.	529 w.	529 w.	531 m.	532 m,
				508 m.	510 m.
	487 m.br.	488 m.br.	488 m.br.	489 s.	492 s.
	438 w.br.	438 w.br.	440 w.br.	442 m.	442 m.